

# Structural and morphological changes in Poly(caprolactone)/poly(vinyl chloride) blends caused by UV irradiation

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**Abstract** Films made from a blend of poly( $\epsilon$ -caprolactone) and poly(vinyl chloride) (PCL/PVC) retained high crystallinity in a segregated PCL phase. Structural and morphological changes produced when the films were exposed to high potency ultraviolet (UV) irradiation for 10 h were measured by UV-Vis spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). They were different to those observed with homopolymer PCL and PVC films treated under the same conditions. The FTIR spectra of the PCL/PVC blend suggest that blending decreased the susceptibility of the PCL to crystallize when irradiated. Similarly, although scanning electron micrographs of PCL showed evidence of growth of crystalline domains, particularly after UV irradiation, the images of PCL/PVC were fairly featureless. It is apparent that the degradation behavior is strongly influenced by the interaction of the two polymers in the amorphous phase.

## Introduction

Ultraviolet (UV) radiation damage is of special relevance to building products routinely exposed to sunlight during use [1]. Although most polymers used in such applications

contain photostabilizers to control photodamage and to ensure acceptable lifetimes of the products the stabilization achieved is never complete and degradation processes occur, albeit at much reduced rate. The photodegradation depends on the presence of chromophores that include structural defects (such as hydroperoxides or carbonyls) in the polymer chain and polymerization catalysts, as well as external impurities (including deliberately added components such as fillers), introduced during the formulation and processing of technical polymers [1].

Polyethylene (PE) and polypropylene (PP) films exposed to solar UV radiation readily lose their extensibility and strength, and this is a particular concern, because these materials are widely used in plastic pipes, greenhouse films, agricultural mulch films, and other outdoors applications. UV degradation of these films is probably initiated by polymer–oxygen charge transfer complexes (CTCs) and the oxidation rate is mainly determined by other radical forming reactions [2].

The current article concerns a family of materials that can be regarded as potential replacements for PE and PP in many outdoor applications, specifically blends of polycaprolactone and poly(vinyl chloride) (PVC). Polycaprolactone (PCL), a semi-crystalline aliphatic polyester, has a relatively low-melting point of 60 °C, which limits its practical applications. However, it can form compatible blends with a wide range of other polymers giving materials with improved thermo-mechanical properties [3]. For example, PCL and PVC are compatible and miscible in the melt in all proportions, and the resulting blends have morphological and mechanical properties suited to certain practical applications. It has been reported that PCL is a very effective plasticizer for PVC [4]. When the melt cools part of the PCL component of PCL/PVC blends with high PCL content separates into a crystalline phase that is usually

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spherulitic [5, 6]. A similar segregation of a crystalline PCL phase appears to occur when solidification occurs from solution. The thickness and arrangement of the PCL crystal lamellae depends on the blend composition; PVC molecules are believed to reside in the amorphous zones between the PCL crystal lamellae [5, 6]. From their Fourier Transform Infrared Spectroscopy (FTIR) measurements on PCL/PVC blends Coleman and co-workers deduced that PCL and PVC display specific interactions in both the melt and the solid form and that this accounts for the apparent compatibility in the amorphous component [5, 7].

Polycaprolactone is an example of a biocompatible, biodegradable, and non-toxic synthetic aliphatic polyester that is completely biodegradable inside the body after interaction with body fluids, enzymes, and cells, and therefore suitable for biomedical applications [8, 9]. However, attention here is focused on the weatherability, in particular the UV resistance, of PCL and its blends. Weatherability is an important characteristic of any polymer and for biomedical applications UV resistance of the polymer is particularly important if UV sterilization procedures are used. Bei et al. [8] studied the photodegradation behavior of polycaprolactone-poly(ethylene glycol) block copolymer (PCL/PEG). Their results indicated that, in a series of UV initiated free radical reactions [8], carbonyl groups in the PCL segments produce  $\text{CO}_2$  and  $\sim(\text{CH}_2)_4\text{CH}_2$  radicals which catalyze the breakdown of the poly(ethylene glycol) segments.

When PVC is exposed to sunlight, it undergoes dehydrochlorination (loss of HCl) and forms polyene sequences— $(\text{CH}=\text{CH})_n$ —with different lengths, although there are no chromophores in the polymer chain. The degradation occurs as the result of the presence of hydroperoxides, carbonyls, unsaturation, and structural irregularities [10, 11]. The carbonyl groups are the most active species of those that begin the photodegradation [12]. Torikai and Hasegawa [13] investigated photodegradation of PVC and proposed the formation of various species, including aldehydes, ketones, and free radicals. A special feature of their study was that they pre-irradiated with short-wavelength radiation (253.7 nm) and afterwards irradiated with monochromatic radiation with various longer wavelengths in the range 275–500 nm, showing that photodegradation was accelerated by the pre-exposure.

The extent to which the physical and mechanical properties of individual components can be modified by blending two or more polymers depends on the exact molecular and morphological arrangements in the solid. In the case of thin films, the morphological features that control their behavior strongly depend on the sample thickness. In very thin films, which consist effectively of a monolayer of macromolecules, the components may become partially miscible and the molecular dispersion is

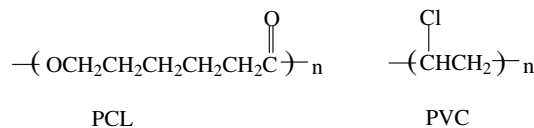
completely different to that in thick samples that have a three-dimensional domain structure [14]. Moreover, the substrate type and solvent used for film preparation also greatly influence polymer morphology. In a relevant study [14] of PVC films blended with small amounts of poly(vinyl acetate) (PVAc), (producing an immiscible PVC/PVAc blend film  $\sim 0.020$  mm thick), the photodehydrochlorination of PVC was monitored by UV-Vis spectroscopy (UV-Vis). During exposure to UV, samples underwent the yellowing, and a broad absorption band in the UV and visible region was observed, caused by the formation of polyene sequences— $(\text{CH}=\text{CH})_n$ —with different lengths. On the basis of absorbance changes at 300 nm, Kaczmarek et al. deduced that PVC dehydrochlorination is hampered by the presence of PVAc [14]. Other changes produced by UV irradiation of this blend were followed by FTIR spectroscopy, which showed the development of bands in the ranges 3,100–3,600 and 1,500–1,800  $\text{cm}^{-1}$ , assigned to OH/OOH (alcohols, peroxides, and carboxyl acids) and  $\text{C}=\text{O}$  stretching vibrations (ketones, aldehydes, esters, acids), respectively [14]. The beneficial stabilization of the second component (PVAc) on the photodegradation of PVC provided part of the motivation for the study presented here.

The current article describes an investigation of photodegradation of PCL and PVC films and films made from a PCL/PVC blend, using UV-Vis Spectroscopy, FTIR, and Scanning Electron Microscopy (SEM).

## Materials and methods

### Chemicals

Poly( $\epsilon$ -caprolactone) was kindly supplied by the Department of Engineering Materials, UFSCar, São Carlos, SP, Brazil. PVC was Norvic, supplied by the Petrochemistry Company of Camaçari, Bahia, Brazil, without additives, and having  $M_w = 145,600$  g/mol. As solvent, 1,2-dichloroethane, p.a., Reagen, was used as received.



### Sample preparation

Films of PCL, PVC and 1:1 blends of PCL and PVC (“PCL/PVC”) were obtained by casting from solutions of PCL and PVC in dichloroethane at room temperature (25 °C) onto a 25-mm diameter glass plate. The films were 90- $\mu\text{m}$  thick and were dried under vacuum for 48 h [15].

## UV exposure

Ultraviolet exposures were conducted using a 400-W mercury lamp for 10 h.

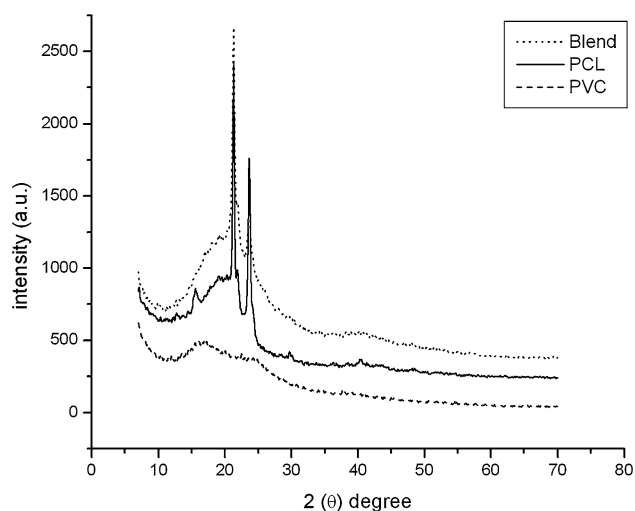
## Film characterization

The films were analyzed using a Philips, X-PERT PLUS X-Ray Diffractometer, employing  $\text{CuK}_\alpha$  radiation (wavelength 0.1542 nm) and using the dedicated software. Two similar films of each sample: as-cast and UV-irradiated (90- $\mu\text{m}$  thick) were used for measuring UV-Vis, FTIR, and SEM. UV-Vis spectra were obtained on a Shimadzu Spectrometer (UV-2401 model), with range 200–800 nm. FTIR spectra were obtained on a Shimadzu Spectrometer (FTIR-8300 model), in the range 4,000–400  $\text{cm}^{-1}$ , with resolution 4  $\text{cm}^{-1}$ . Films were put onto aluminum holders and sputter-coated with gold in a vacuum chamber (Balzers, MED 010) prior to SEM observation in a Zeiss SDM-940A, using 5 keV electrons.

## Results

### X-ray diffractograms

Figure 1 gives X-ray diffractograms for the various samples. The PVC film shows broad absorptions at  $2\theta = 17$  and  $24^\circ$ , consistent with a predominantly amorphous film with a small fraction of crystalline or quasi-crystalline material, whereas PCL shows relatively sharp crystal reflections, superimposed on a diffuse reflection, attributed

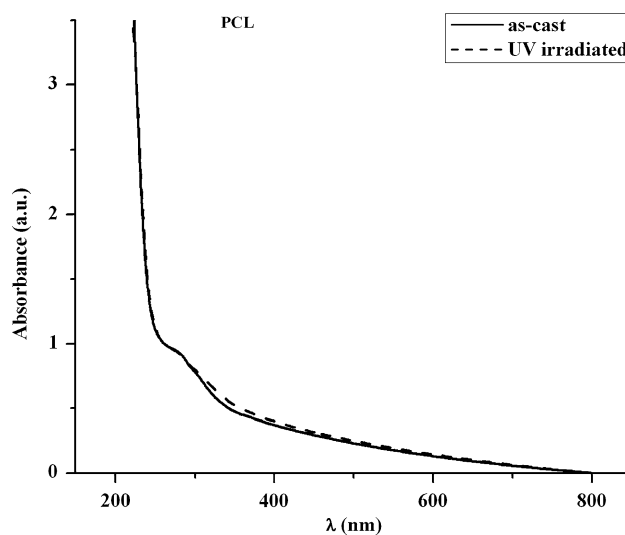


**Fig. 1** X-Ray diffractograms for PCL (middle trace), PVC (bottom trace), and PCL/PVC blend films (top trace). For clarity, the diffractograms have been displaced vertically with respect to one another

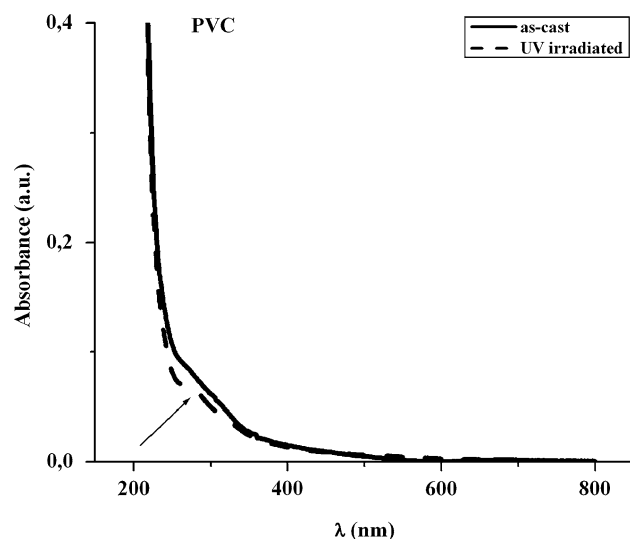
to the amorphous phase. The crystal phase of PCL is orthorhombic with cell parameters  $a = 0.748$  nm,  $b = 0.498$  nm,  $c = 1.729$  nm [16, 17]. The strongest reflections are for (110) and (200) which, for  $\text{CuK}_\alpha$  radiation, appear at  $2\theta = 21.4^\circ$  and  $23.8^\circ$ , respectively. These are the reflections observed in the PCL diffractogram in Fig. 1. It should be noted that some  $\{hkl\}$  reflections overlap with the (200) reflection [16]. Strong evidence of crystallinity is also observed in the diffractogram of the 1:1 blend. It appears that part of the PCL phase has segregated and crystallized under the conditions described in the “Sample preparation” section above. The PCL/PVC (110) and (200) peaks in Fig. 1 superimpose exactly over those for PCL and the main difference between the diffractograms is that the broad non-crystalline diffraction peaks are stronger for PCL/PVC than for PCL. This may come from a mixed PCL–PVC phase or from segregated PCL and PVC domains.

### UV-Vis

The UV-Vis spectrum of PCL (Fig. 2) possessed a weak shoulder at 250–300 nm which was attributed to the  $n \rightarrow \pi^*$  transition of the ester carbonyl and showed negligible change on irradiation. Prior to irradiation the spectrum of the unirradiated PVC films showed a similar, but less distinct shoulder (Fig. 3). It is unlikely that this is due to a carbonyl absorption because the corresponding IR spectrum shows no evidence of absorption at  $\sim 1,740$   $\text{cm}^{-1}$ . An alternative assignment is to the trace amounts of conjugated double bonds, as suggested by Torikai and Hasegawa [13]. The  $n \rightarrow \pi^*$  transition of the ester carbonyl has a very high extinction coefficient ( $10^3$  times that of the

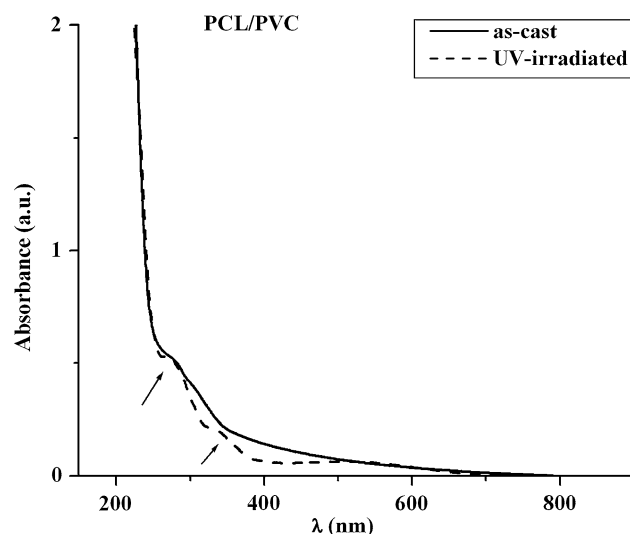


**Fig. 2** UV-Vis spectra for PCL films

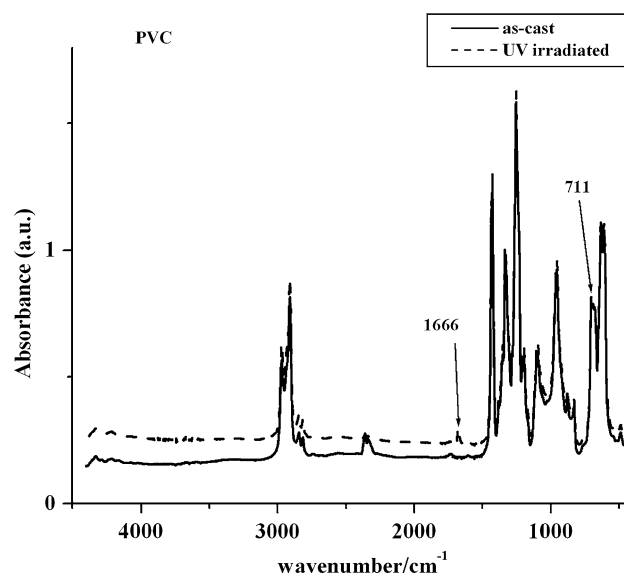


**Fig. 3** UV-Vis spectra for PVC films

carbonyl absorption of the  $\pi \rightarrow \pi^*$  transition [18]), and trace amounts of impurity or of dehydrochlorination would be sufficient to give rise to the absorption. On irradiation the degree of conjugation is expected to increase and cause the extended chromophore to absorb at longer wavelengths. This is consistent with the small changes observed after 10-h irradiation. The UV-Vis spectra for the PCL/PVC blend (Fig. 4) also shows evidence of a decrease in absorption on UV radiation—particularly at  $\sim 300$  and  $\sim 400$  nm. However, in this case, sharper bands remain at 280 and 350 nm (see arrowed regions in Fig. 4). The residual band at 280 nm may be due to the carbonyl absorption of the PCL component. Assignment of the residual absorption at  $\sim 350$  nm is less certain, but one possibility is that it is due to the weak



**Fig. 4** UV-Vis spectra for PCL/PVC films



**Fig. 5** FTIR spectra for PVC films

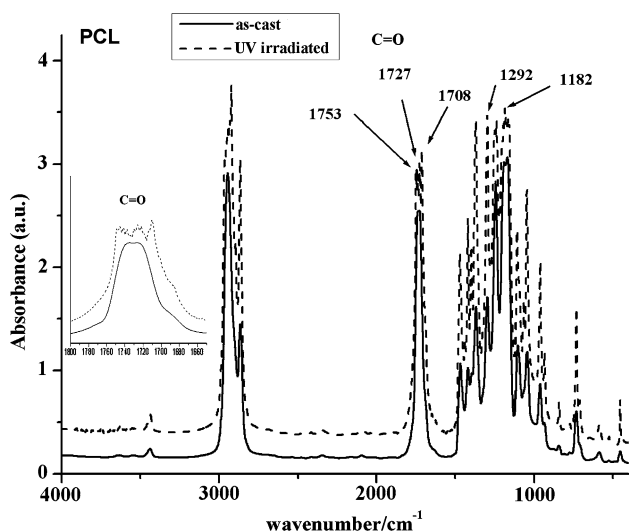
$n \rightarrow \pi^*$  transition of a  $C = C - C = O$  group (the stronger  $\pi \rightarrow \pi^*$  absorbs at  $\sim 220$  nm and would not be observed).

#### FTIR

The IR spectrum for the PVC film is shown in Fig. 5. UV exposure caused only small changes in the spectrum; the principal changes are at the positions indicated with arrows in Fig. 5. A very weak band centered at  $1,666$   $\text{cm}^{-1}$  which develops on irradiation may be due to generation, by dehydrochlorination, of a few unconjugated  $C = C$  groups. No absorption due to carbonyl groups could be detected. An increased IR absorption at  $711$   $\text{cm}^{-1}$ , on the high frequency side of the band originally centered near  $683$   $\text{cm}^{-1}$ , probably indicates a small change in the conformation of the  $C-Cl$  groups since, as tabulated by Voyiatzis et al. [19], the exact frequency of the  $C-Cl$  stretching frequency of PVC varies with different molecular conformations, e.g., it increases from  $605$   $\text{cm}^{-1}$  for a syndiotactic long trans sequence to  $708$   $\text{cm}^{-1}$  for a heterotactic triad. Changes in the  $\text{CH}_2$  wag or bending modes at around  $1,335$  and  $1,430$   $\text{cm}^{-1}$ , respectively, were negligible.

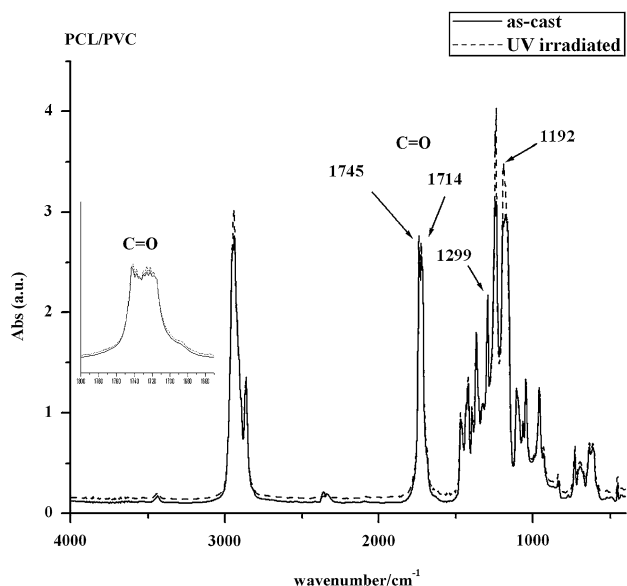
Although the complexity and intensity of the spectra precluded quantitative analysis of these changes, the intensity of the  $1,292$   $\text{cm}^{-1}$  band relative to the  $1,182$   $\text{cm}^{-1}$  band appears to have doubled on irradiation.

By contrast, UV irradiation caused relatively large changes in the IR spectrum of the PCL film (Fig. 6). The strong  $1,727$   $\text{cm}^{-1}$  absorption of carbonyl groups present in the initial unirradiated polymer broadened. The high absorbance of this broadened band limits precise location of the constituent peaks but the maxima near  $1,753$  and



**Fig. 6** FTIR spectra for PCL films. Carbonyl bands are shown in the inset

1,708 cm<sup>-1</sup> are paralleled by the peaks at 1,737 and 1,724 cm<sup>-1</sup>, assigned to carbonyl groups in the amorphous and crystalline phases of PCL–PDMS–PCL/PVC [4]. (Karal et al. attributed the different frequencies to the effect of the poly(dimethyl siloxane) and the solvent used to prepare the films.) On irradiation, the strength of the 1,708 cm<sup>-1</sup> band, relative to the 1,753 cm<sup>-1</sup> band appears to increase, as might be expected if the polymer crystallinity had increased. Increased absorption at 1,292 cm<sup>-1</sup>, assigned to the combination of the C–C and C–O stretching modes in the PCL crystalline phase, relative to the



**Fig. 7** FTIR spectra for PCL/PVC films. Carbonyl bands are shown in the inset

absorption at 1,182 cm<sup>-1</sup>, assigned to the amorphous phase [20] supports this interpretation.

In the spectrum for the PCL/PVC blend (Fig. 7) the PCL carbonyl bands are shifted (compared to the pure PCL). This is consistent with an interaction of the  $\alpha$ -hydrogen of PVC with the carbonyl groups of the PCL (C = O...H–C–Cl) [4, 21], which would assist miscibility in the amorphous phase of the blend. On irradiation of the PCL/PVC blend, any changes in the relative intensity of the 1,745 and 1,714 cm<sup>-1</sup> bands (assigned to the amorphous and crystalline phases, respectively) are much smaller than for the PCL. Other changes occurred at 1,400 cm<sup>-1</sup> (C–O vibration) and 711–669 cm<sup>-1</sup> (C–Cl vibration) but they were significantly less than those induced in pure PCL. Overall, the IR spectra suggest that blending has decreased PCL’s susceptibility to crystallize when UV irradiated.

**SEM**

The unirradiated PVC films were fairly featureless, showing only small pinholes/bubbles, characteristic of solution-cast polymer films and usually attributed to solvent evaporation (Fig. 8(a)). After UV irradiation the film showed very strong degradation with evidence of surface erosion (Fig. 8(b)).

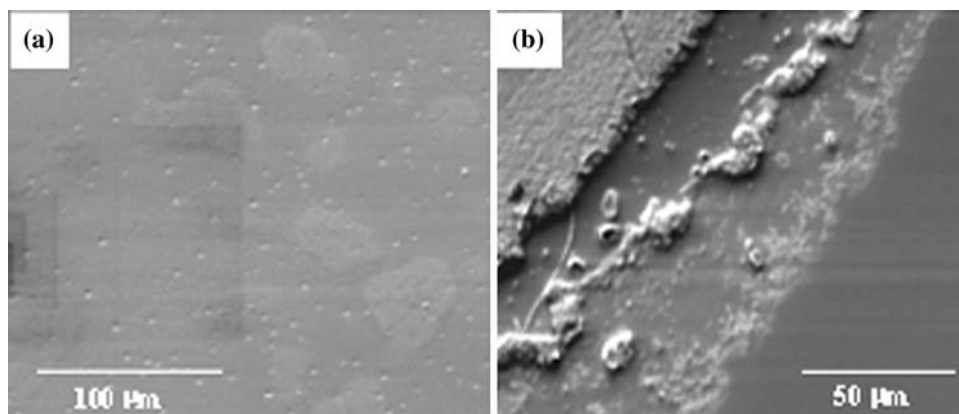
A quite different morphology was revealed in the SEM of as-cast PCL (Fig. 9(a)). The appearance is that of growth of crystalline domains from heterogeneous nucleation centers followed by impingement to generate polyhedral morphology; some pinholes are still in evidence. After UV irradiation, sheaf-like features were revealed in the domains, presumably the result of oxidative etching to reveal crystal lamellae, confirming that the structures were spherulites (Fig. 9(b)). X-ray diffraction (Fig. 1) provided evidence of PCL crystallinity.

The morphology of the as-cast PCL/PVC blend resembled that of the PVC film with pinholes as the major feature (Fig. 10(a)). After UV irradiation some large isolated craters appeared; elsewhere the appearance was one of uneven, shallow, etching of the surface (Fig. 10(b)).

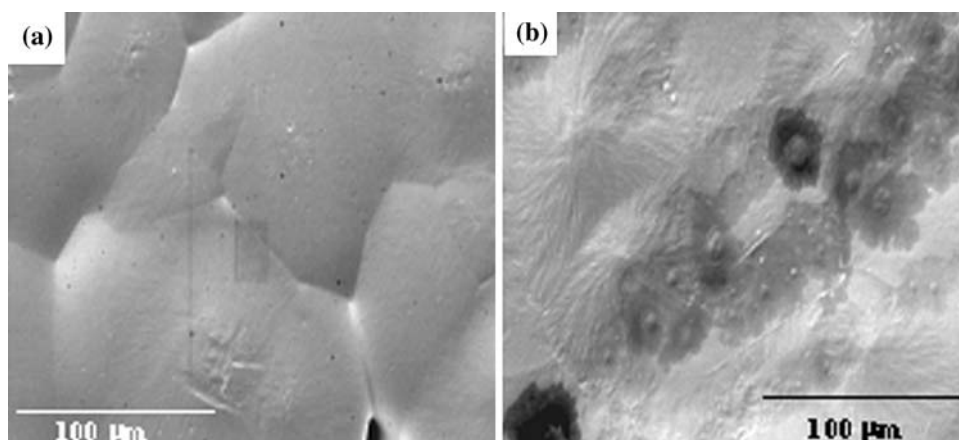
**Discussion**

The X-ray diffraction results show clearly that the PCL/PVC blend was very crystalline. This contrasts with the observations reported by Zhang and co-workers [16]. Although they do not emphasize the point, their examples of the X-ray analyses with unstrained samples do not indicate any crystallinity even though their blends are richer in PCL than those used by the present authors. However, Karal [4] summarizes work by a number of

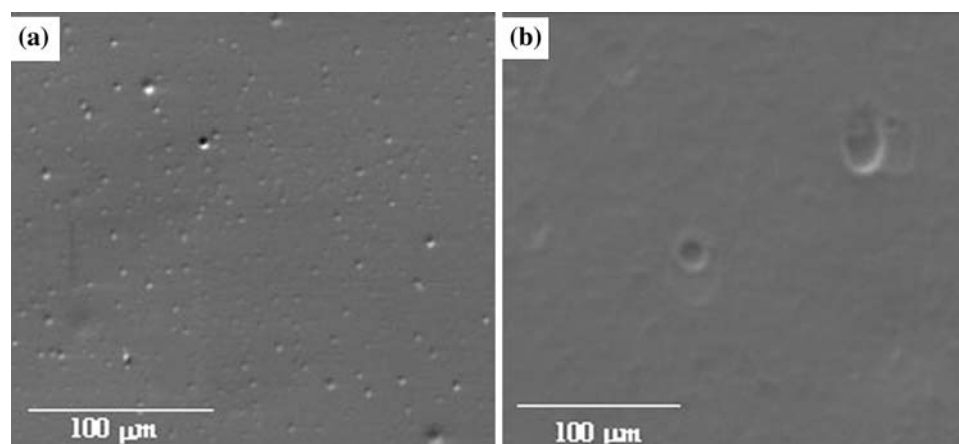
**Fig. 8** SEM of PVC films (a) as-cast, unirradiated. (b) UV irradiated



**Fig. 9** SEM of PCL films (a) as-cast, unirradiated (b) UV irradiated



**Fig. 10** SEM of PVC/PCL 1:1 films (a) as-cast, unirradiated (b) UV irradiated



authors that indicates that the blends are essentially amorphous, when the PVC concentration exceeds a 2:1 molar ratio. Our 1:1 (by weight) sample corresponds to a PVC/PCL molar ratio of 1.8:1, i.e., it is just below the critical value. Most probably, the polymer molecular weight and both the film preparation method and thickness influence the film crystallinity. Zhang and co-workers found that with their initially amorphous PVC/PCL blends with w/w compositions 40/60, 30/70, and 20/80, (corresponding to molar ratios of 1.2:1, 0.8:1, and 0.5:1), crystals

grew when film samples were held at room temperature under tensile strain for extended periods. It seems that the solution casting method used in the current investigation allows advanced crystalline development within the films without any external mechanical intervention.

The SEM images before and after exposure indicate that homopolymers PVC and PCL suffered the most drastic changes. PVC showed very strong erosion, whereas PCL displayed severe etching of the amorphous zones to reveal the sheaf-like lamellae within the spherulites.

As indicated above the main conclusion from the infrared studies, especially from the changes in the carbonyl region of the spectrum is that the photochemical changes induced in the PCL were greater than those induced in the PCL/PVC blend and corresponded to enhanced crystallinity, as suggested by the micrographs of the irradiated PCL film. The absence, from PCL/PVC of the very weak absorption, at  $\sim 1,667\text{ cm}^{-1}$ , taken as possible evidence for isolated  $\text{C}=\text{C}$  groups in PVC, cannot be taken as evidence of decreased reactivity of the PVC component because such a weak absorption would easily be obscured by the strong absorption of (ester) carbonyl groups in the blend.

It is generally accepted that oxidative attack occurs predominantly in the amorphous phase of semi-crystalline polymers, partly because the photo-active chromophores are normally rejected from the growing crystals and partly because oxygen can diffuse more readily through the amorphous zones and is far less abundant, if not excluded, from the crystal domains. Oxygen diffusion may be the more important factor for PCL, in which the chromophores are an intrinsic part of the chain, and not, as with peroxide groups in polyalkenes, an extrinsic addition. The lower level of surface damage of the PCL/PVC blend seems to indicate some measure of mutual protection, as has been seen in thermally treated blend, in which the presence of PCL inhibits the thermal degradation of PVC (Campos and Martins-Franchetti, [22]). In another study it was shown that the carbon dioxide produced when PCL/PVC was exposed to UV was less than with PCL or PVC when exposed under the same conditions [23].

## Conclusions

Part of the PCL formed a crystalline phase within the 1:1 blend with PVC, just as in the PCL homopolymer. The remaining PCL together with the PVC formed an amorphous phase. It is not known to what degree molecular mixing of the two component polymers occurred in this phase, but it is known that these two polymers undergo excellent molecular mixing in the melt. The photodegradation of the PCL/PVC blend when exposed to UV irradiation was significantly influenced by interaction between the two components. The changes caused by UV exposure that were observed in the PCL/PVC blend were different to those that would be obtained from a simple

addition of the changes that occurred in the homopolymers when treated in the same manner. Coupled with results from another study in which the carbon dioxide reaction product was monitored [23], it seems that the blend is more resistant to photodegradation than the component polymers.

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