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Photodegradation of polycaprolactone/poly(vinyl chloride) blend

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Abstract

The photodegradation of a 1:1 w/w blend of polycaprolactone and poly(vinyl chloride) has been studied by following carbon dioxide emission during UV exposure. Similar measurements were performed for polycaprolactone and poly(vinyl chloride) homopolymers which were prepared and irradiated in the same way. It was found that the blend gave lower CO_2 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.

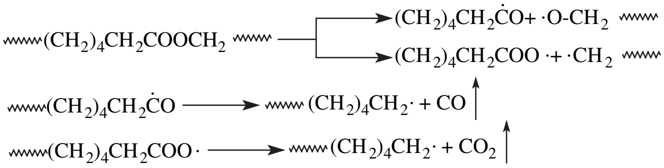
Keywords: Photodegradation; PVC; PCL; Blend

1. Introduction

Polycaprolactone (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 polycaprolactone/poly(ethylene glycol) block copolymer (PCL/PEG). They proposed that the carbonyl groups present in the PCL photodegraded to form CO_2 and $-(CH_2)_4CH_2\bullet$ radicals which then broke down the poly(ethylene glycol) by a series of free radical reactions (Scheme 1).

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 TiO_2 pigmented films can be used



Scheme 1. PCL photodegradation reactions.

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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 min. 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 film thickness was measured with a manual thickness gauge (Mitutoyo, Japan). The UV spectra of PCL and blends were measured from 200 to 800 nm using a Shimadzu 2401 spectrometer. X-ray diffraction measurements were made with CuK$_\alpha$ radiation (wavelength 0.1542 nm) 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 to a CaF$_2$ 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 → π* transition of the carbonyl group.

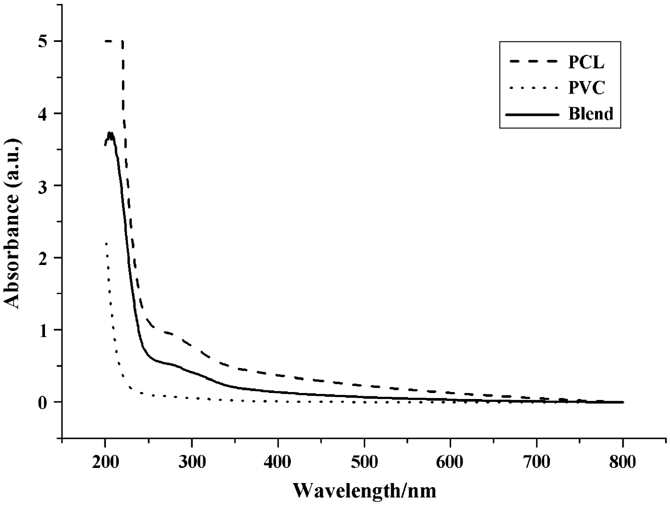

Fig. 1. Transmission spectra of 100 μm films of polycaprolactone (PCL); poly(vinyl chloride) (PVC) and of a 50:50 blend of the 2 components.

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 $2\theta \sim 17°$ and 24°, characteristic of a predominantly amorphous film with a small crystalline or quasi-crystalline fraction (Fig. 2). The PCL film showed relatively sharp peaks at positions close to the orthorhombic PCL reflections at $2\theta = 21.4°$ and 23.8° [13,14], and an amorphous halo under the crystalline reflections. The ratio of the crystalline and amorphous reflections indicated significant

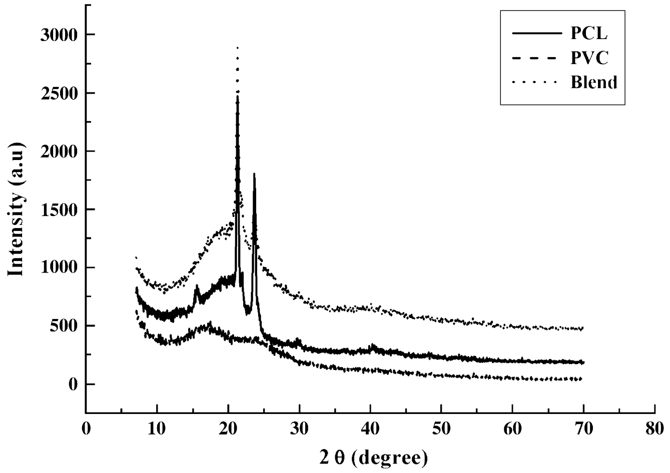

Fig. 2. X-ray diffractograms of 100 μm films of polycaprolactone (PCL) (middle curve); poly(vinyl chloride) (PVC) (bottom curve) and of a 50:50 blend of the two components (top curve). For clarity, the diffractograms have been displaced vertically with respect to one another.