

Two-dimensional correlation analysis study of the photo-degradation of poly(ethylene terephthalate) film

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ABSTRACT

The photo-degradation of poly(ethylene terephthalate) (PET) film was investigated in detail using ultraviolet–visible (UV–visible) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and two-dimensional (2D) correlation analysis. The analysis of 2D FTIR correlation spectra led to the identification of photoproducts: esters, peresters and benzoic acids. The photo-degradation of PET films strongly influences the spectral changes of the ester linkages as well as the CH₂ groups adjacent to the ester groups. In addition, the spectral change of CH₂ groups occurred before that of terephthalate groups.

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1. Introduction

Photovoltaic (PV) technologies are one of cleanest power sources since it does not produce CO₂ and toxic gases, such as SO_x and NO_x. The basic energy producing unit in PV technologies is the PV cell, which captures solar radiation and converts it directly into electrical energy. A PV module consists of many jointly connected solar cells which are packaged between a backsheet on the bottom and a tempered-glass window on the top. The backsheet is the outermost layer of the PV module and is therefore designed to protect the inner components of the module (e.g. photovoltaic cells and electrical components) from external stresses such as ultra-violet (UV) light, moisture, and bad weather. In order to accomplish this, the backsheet must be a organic polymer material that has high robustness and dielectric properties.

Because of the desirable properties of poly(ethylene terephthalate) (PET) films (see Fig. 1), recently, they have been of wide interest in both academia and the photovoltaic (PV) modules industry. Indeed, PET is commonly used as packaging films, synthetic fibers, bottles for beverage and food, and engineering plastic components, owing to their excellent thermal and mechanical properties, high chemical resistance, and low gas permeability [1–3]. However, PET still has some undesirable properties:

for example, ease of degradation by UV irradiation, pilling, low moisture regain, generation of static charges and poor adhesion to metals.

Among the shortcomings of PET film, the degradation behavior is a big issue to apply PET as a solar cell backsheet. In order to understand this process, both the degradation and stabilization of PET and PET copolymer films have been investigated throughout the years [4–8]. Several photo-degradation pathways have been proposed to elucidate photo-degradation mechanism of PET and poly(butylene terephthalate) (PBT) films by UV irradiation in the presence of oxygen [9–14]. In addition, much effort has been exerted to identify the photoproducts from the photo-degradation of PET and PBT films [8–10]. The photo-degradation of PBT film induced oxidation of the methylene group in the α -position of the ester band and the radicals generated from this process can lead to formation of esters, peresters, aliphatic acids and aromatic acids [9,10]. However, the photo-degradation mechanism of PET and PBT films is not clearly studied due to the complexity of the photo-degradation processes.

As described in our previous reports [15,16], 2D correlation spectroscopy can be employed to analyze the molecular interactions between spectral peaks as well as to investigate the molecular segmental motions in detail. Furthermore, it is also possible to determine the sequence of the spectral peak emergence.

In this study, the two-dimensional (2D) correlation spectroscopic analysis was extended to closely examine the photo-degradation behavior of PET film. The photo-degradation of PET films was characterized using ultraviolet–visible (UV–visible)

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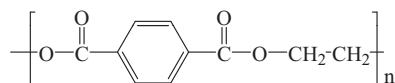


Fig. 1. Chemical structure of poly(ethylene terephthalate) (PET).

spectroscopy, Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials and measurement

The biaxially oriented PET film (thickness 38 μm) without photo-stabilizer was obtained from Kolon Industries, Inc. Prior to the UV light exposure, PET films were sonicated for 5 min in diethyl ether and dried under a stream of nitrogen to remove any particulate.

PET film was irradiated by polychromatic UV light (500 W) with an optical filter (250–380 nm) at room temperature in air. The distance between PET film and lamp was 10 cm. UV–visible absorption spectra were obtained as a function of the exposure time using a Sinco UV–visible spectrophotometer. The thermal stability was measured in the temperature range of 50–800 $^{\circ}\text{C}$ using a thermogravimeter (model TGA7, Perkin-Elmer). During the measurements, the system was purged with dry nitrogen gas at a flow rate of 100 cc/min and a ramping rate of 10.0 $^{\circ}\text{C}/\text{min}$. FTIR spectroscopic measurements were carried out on a BOMEM DA8 FTIR spectrometer equipped with Golden gate diamond ATR (Specac). IR spectra were recorded at 4 cm^{-1} resolution with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector under vacuum. To ensure a high signal-to-noise ratio, 256 interferograms were co-added for each measurement.

The 2D correlation spectra were obtained using an algorithm based on a numerical method developed by Noda [17–20]. The 2D correlation analysis was then performed after baseline correction. A subroutine named KG2D written in Array Basic language (GRAMS/386; Galactic Inc., NH) was employed in the 2D correlation analysis [21].

3. Results and discussion

Fig. 2 shows the UV–visible absorption spectra of PET film irradiated by UV light at various irradiation time. Before irradiation, PET film exhibits saturated absorption by benzene rings, conjugated

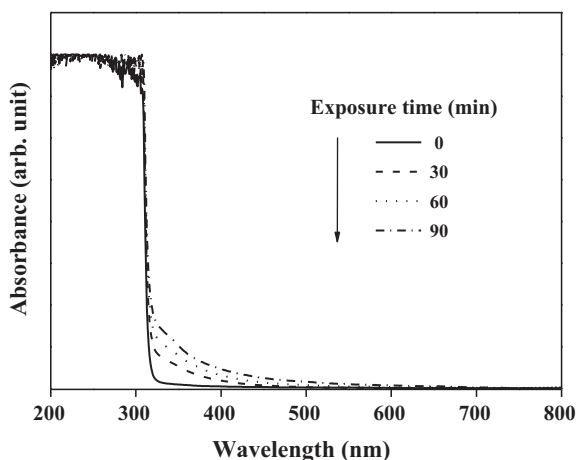


Fig. 2. UV–visible spectra of PET film irradiated with UV light at various irradiation time.

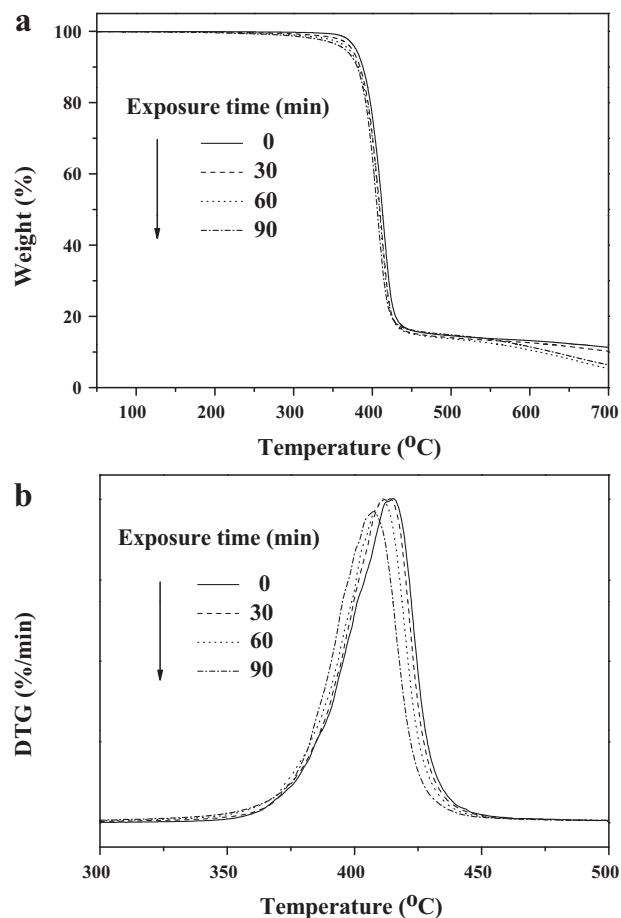


Fig. 3. (a) TGA thermograms and (b) derivatives of TG (DTG) curves for PET film irradiated with UV light at various irradiation time, which were measured at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

ester groups of PET and film thickness in the wavelength range lower than 315 nm. As irradiation time increased, new absorption bands appeared in the region of 320–500 nm and also the intensities of absorption bands increased. This result coincides with the previously reported results [13,14], which can be attributed to the presence of photoproduct formed during the photo-degradation of PET film.

Fig. 3 plots the TGA/DTG (derivative of thermogravimetry) thermograms of virgin PET film and PET films at various UV light irradiation time. To investigate obvious thermal stability of before and after UV light irradiated PET films, the DTG curves of PET films in the region of 300–500 $^{\circ}\text{C}$ is shown in Fig. 3(b). The virgin PET film was found to be thermally stable up to around 350 $^{\circ}\text{C}$ when one-step thermal degradation takes place as displayed in Fig. 3(a). However, the degradation temperature was slightly decreased with increasing irradiation time. It is well known that during PET photolysis the main degradation event is chain scission, leading to a decrease in molar mass and evolution of volatile products (like CO and CO₂) [6]. These decreasing in the thermal stability of UV light irradiated PET films might be attributed to the main chain scission by photolysis. Fig. 3(b) exhibits the DTG curves of PET films in the region of 300–500 $^{\circ}\text{C}$. As shown in Fig. 3(b), the initial degradation temperature and maximum degradation rate were decreased with increasing UV light irradiation time. These results are consistent with their UV absorption spectra at various irradiation time. In addition, the DTG curves have single peak, which means that a single step reaction takes place during pyrolysis of the virgin PET film and UV light irradiated PET films.

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