CHAPTER III

EXPERIMENT

3.1 Instrument

1. Nicolet Magna 750 FT-IR spectrometer and NICPLAN™ infrared microscope
2. Nicolet NXR 9650 FT-Raman spectrometer
3. Hamamatsu L5662-01 UV spot light
4. Fisher scientific oven Model 516G

3.2 Accessories

1. Conventional ATR accessory: Single reflection attenuated total reflection (SATR) accessory (the Seagull™, Harrick Scientific, USA) equipped with a ZnSe IRE at the angle of incident of 45 degrees)
2. Homemade diamond μATR probe developed by Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
3. UV fiber optic

3.3 Chemicals and material

1. Acetone 99.8 % Merck
2. Lint free paper (Kimwipes)
3. PET film
4. Staple PET fiber
5. Spin draw yarn (SDY) of PET from Teijin polyester
6. Draw texture yarn (DTY) of PET from Teijin polyester

3.4 Sample preparation

3.4.1 PET film

A thick PET film was cleaned by deionized water (DI) and wiped by lint free paper (Kimwipes). The cleaned film was cut into small pieces. A 5x5x2 millimeters PET film was employed for the diamond μATR analysis. The PET sample was kept at room temperature until being analyzed.

3.4.2 Staple PET fiber

Staple PET fibers (10-20 fibers) were placed on a hole on a polymer substrate. The hole was made by pressing the polymer substrate against the diamond IRE. The staple was prepared as shown in Fig. 3.1.

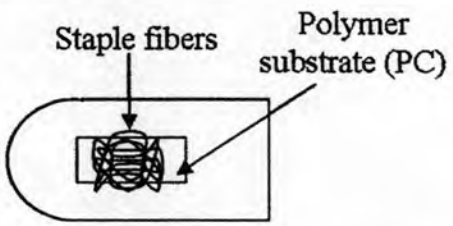


Fig. 3.1 Sample preparation of staple PET fibers.

3.4.3 PET filament

Both spin draw yarns (SDY) and draw texture yarns (DTY) were prepared and were placed on the holder made of small wire. The samples were rolled around the holder (about 10-20 cycles) and placed on a hole on polymer substrate. The PET filament was prepared as shown in Fig. 3.2.

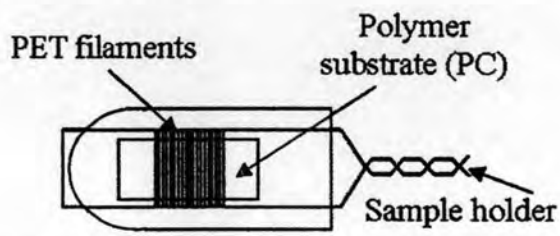


Fig. 3.2 Sample preparation of PET filaments.

3.5 UV irradiation techniques

3.5.1 UV irradiation condition

Instrument	Hamamatsu L5662-01 UV spot light
Source	Mercury-Xenon Lamp
Filter	Hamamatsu UV filter A6562-03
Type	365 nm
Wavelength range	300-450 nm
Light intensity	3500 mW/cm^2

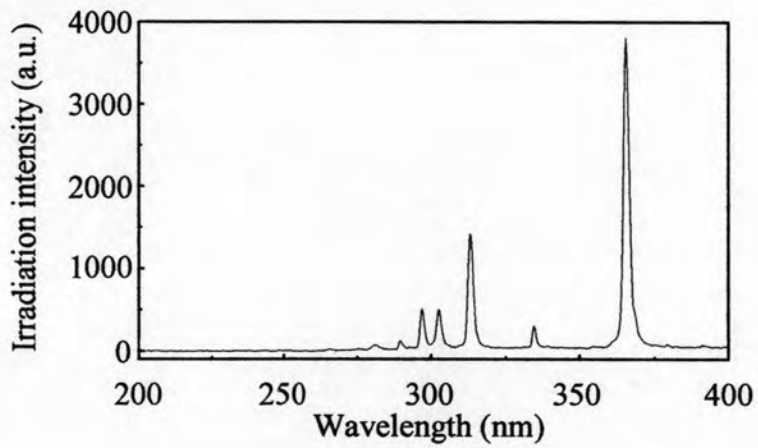


Fig. 3.3 UV spectrum of Hamamatsu L5662-01 UV spot light.

3.5.2 UV transmission irradiation

The Hamamatsu UV spot light was equipped with fiber optic for UV irradiation. The PET samples were prepared and placed on a glass slide. The distance spacing from fiber optic to the sample surface was carefully controlled at 5 mm. The UV radiation from fiber optic was irradiated on the PET specimen with a normal incidence. The irradiation times were controlled at 1, 10, and 30 minutes. The irradiated samples were removed and analyze by the spectroscopic technique after UV irradiation was completed. The UV transmission irradiation of PET as shown in Fig. 3.4

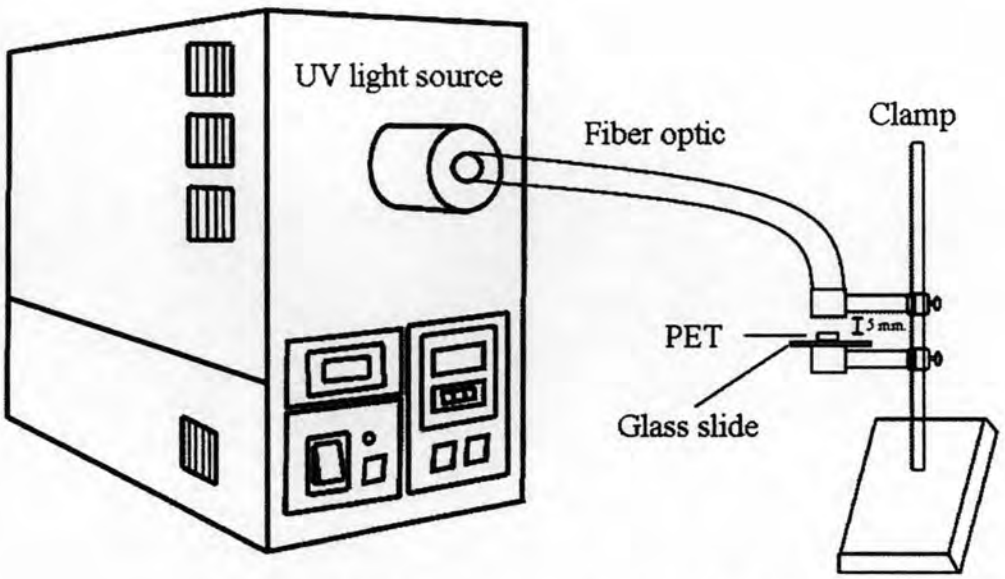
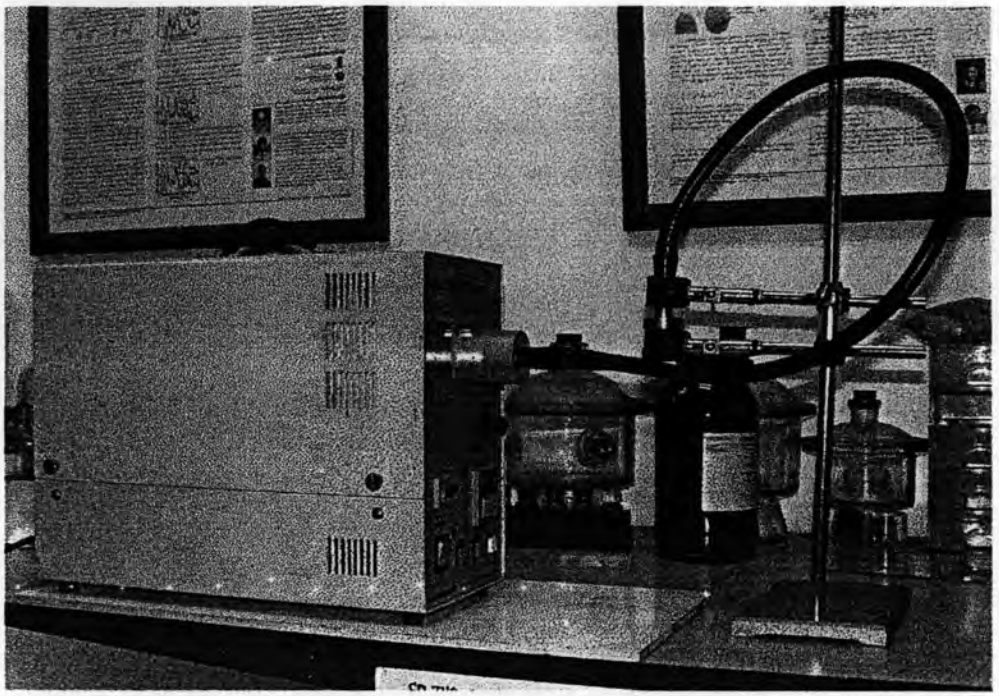


Fig. 3.4 UV transmission irradiation of PET.

3.5.3 UV evanescent field irradiation

A PET sample was prepared and placed at the culet of a 0.1445 ct natural diamond type IaB. The diamond that was mounted in the homemade μATR probe served as an internal reflection element (IRE) for UV irradiation and for ATR FT-IR measurement. The culet of the diamond was penetrated into the film by pressing the film against the diamond IRE. The degradation was initiated by irradiating the UV radiation through the table facet of the diamond IRE. This process induced the UV evanescent field at the interface between diamond IRE and the PET surface. As the UV evanescent field irradiation was completed, the irradiated PET sample was immediately analyzed by an infrared microscope without removing the sample. The specimen was kept for further characterization with FT-Raman spectroscopy. The UV evanescent field irradiation of PET and μATR probe was shown in Fig. 3.5 and 3.6, respectively.



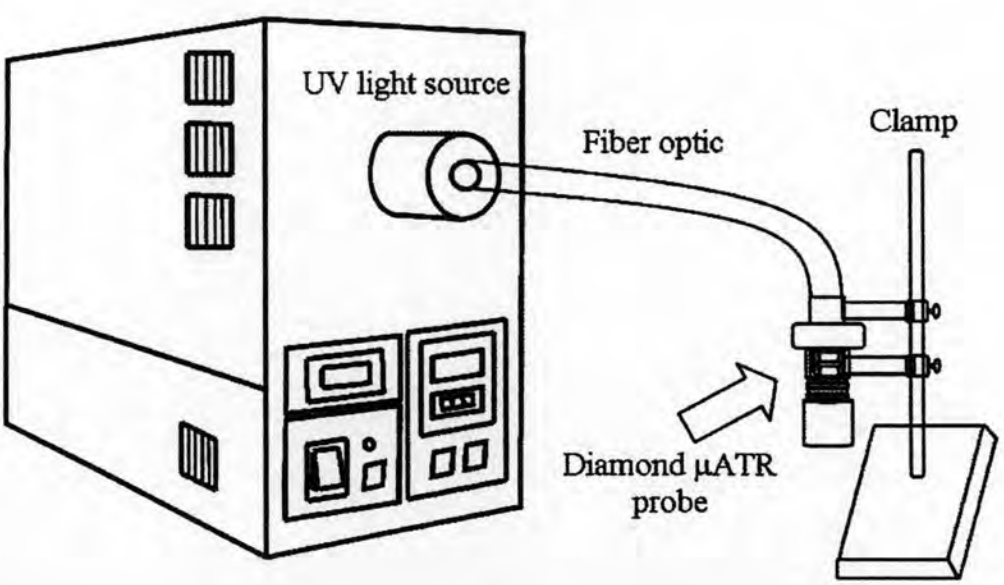


Fig. 3.5 UV evanescent field irradiation setup.

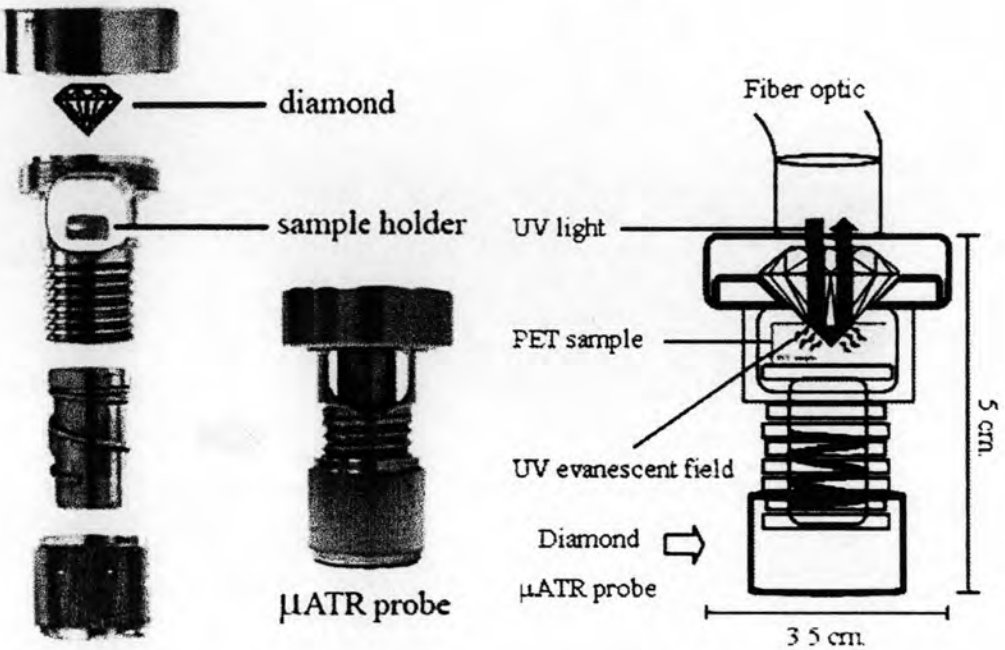


Fig. 3.6 μATR probe for UV evanescent field irradiation.

3.6 Characterization conditions

Nicolet Magna 750 FT-IR spectrometer and NICPLAN™ Infrared microscope

Instrument Setup

Model	Nicolet Magna 750 FT-IR spectrometer and NICPLAN™ Infrared microscope
Source	Standard Globar™ Infrared High Source
Beam splitter	KBr
Detector	Mercury-Cadmium-Telluride (MCT)

Spectra Acquisition Parameter

Resolution	4 cm^{-1}
Gain	Auto
Aperture size	50 μm
Number of scans	128 scans
Spectra format	Absorbance
Spectra range	730-4000 cm^{-1}

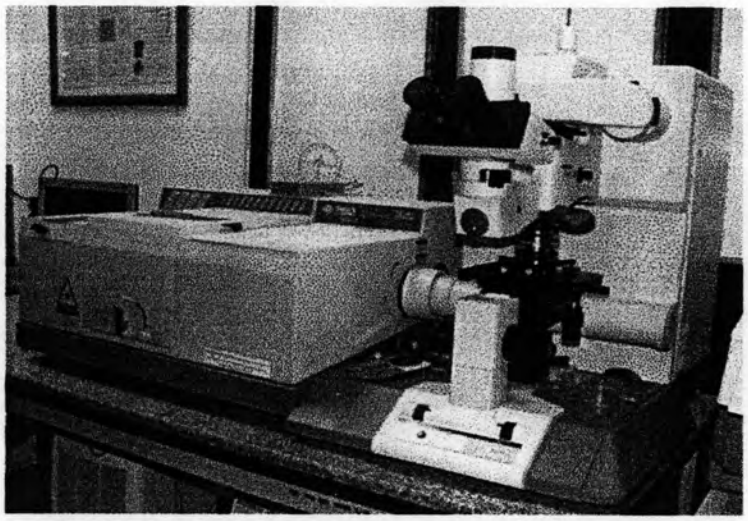


Fig. 3.7 Nicolet Magna 750 FT-IR spectrometer and Nicplan FT-IR microscope.

Nicolet NXR 9650 FT-Raman spectrometer

Instrument Setup

Model	Nicolet NXR 9650 FT-Raman spectrometer
Source	Laser source at 1064 nm
Beam splitter	CaF_2
Detector	Indium gallium arsenide (InGaAs)

Spectra Acquisition Parameter

Power set up	0.951 W
Resolution	8 cm^{-1}
Gain	8.0
Aperture size	50 μm
Number of scans	128 scans
Spectra format	Raman intensity
Spectra range	200-3500 cm^{-1}

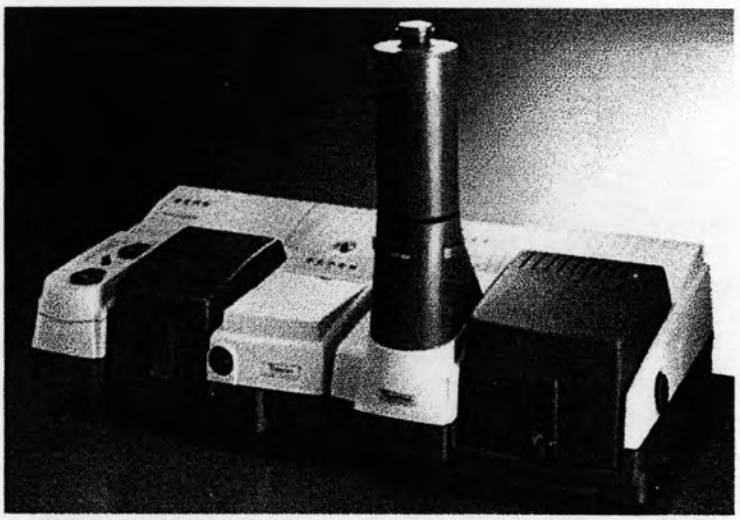


Fig. 3.8 Nicolet NXR 9650 FT-Raman spectrometer.

3.7 Characterization techniques

3.7.1 ATR FT-IR spectroscopy

Conventional ATR

Conventional ATR FT-IR spectra in the mid-infrared region were collected by a Nicolet Magna 750 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. The PET sample (5 x 5 x 0.5 mm) was attached with a 25 mm hemispherical ZnSe IRE. The ZnSe IRE was employed of all ATR FT-IR spectral acquisitions. To acquire an ATR spectrum, a PET sample was placed on flat surface of the IRE while an external force was applied onto the specimen against the IRE in order to ensure a good contact.

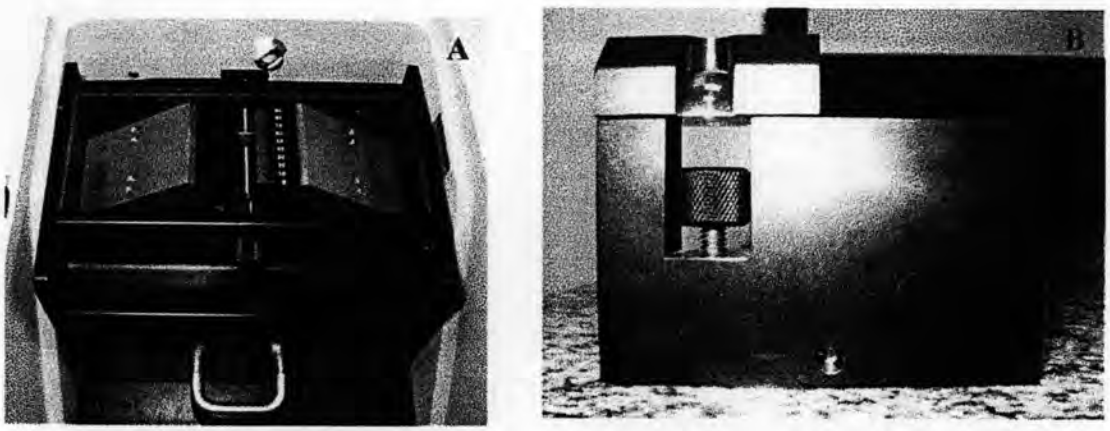


Fig. 3.9 Conventional ATR accessory: (A) Single reflection attenuated total reflection (SATR) accessory (the Seagull™, Harrick Scientific, USA) and (B) ZnSe IRE holder.

Homemade diamond μATR probe

For the ATR FT-IR spectral acquisition using infrared microscope, a gem quality round brilliant cut natural diamond type IaB (0.1445 carat) was employed as an IRE. The defect free diamond was mounted onto a homemade μATR probe. The homemade accessory has a sample holder where solid sample can be brought into an optical contact with the culet of the diamond IRE. An infrared radiation from the infrared microscope was coupled into the diamond of the μATR probe while the transflectance radiation was collected via the 15 X Cassegrain objectives. The infrared evanescent field radiation is generated at the pavilion facet interacts with the diamond attached to the PET. Before the attached PET was collected, the diamond spectrum has been collected for spectra subtraction. The specularly reflected radiation from the table facet of the diamond was employed as a background for all the acquired ATR FT-IR microscope spectra. A spectrum of un-irradiated PET was collected by ATR FT-IR until the observed spectra were unchanged. In the case of UV evanescent field irradiation, ATR FT-IR spectra of the irradiated PET was immediately collected after the UV irradiation without removing the sample. The ATR FT-IR microscope characterization was shown in Fig. 3.10.

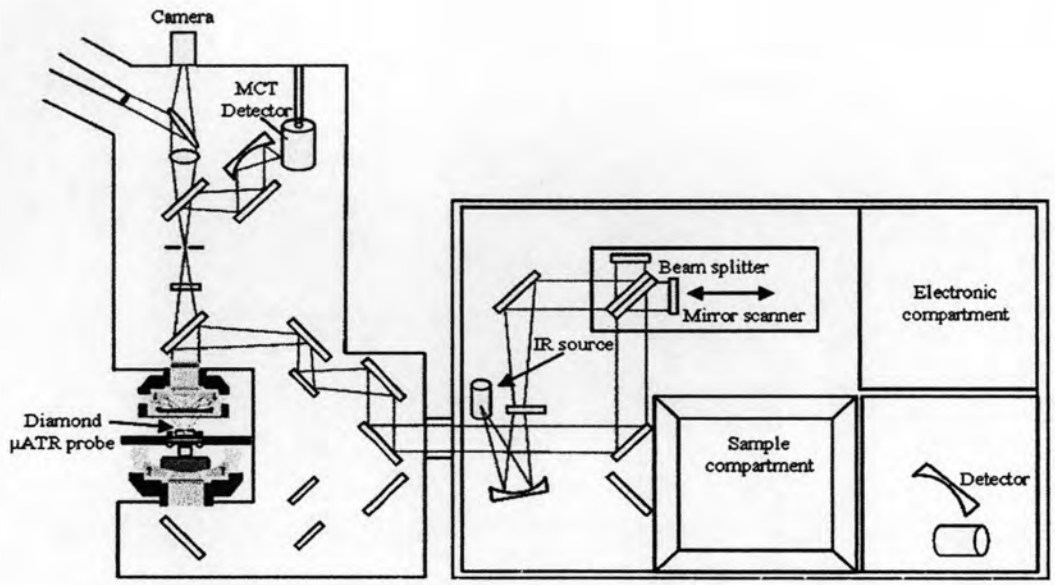


Fig. 3.10 ATR FT-IR spectra acquisition with a μATR probe.

3.7.2 Curve fitting

The observed ATR FT-IR spectra were resolved by the curve fitting algorithm in the OMNIC software. The fitting peak strategy of irradiated PET which are carbonyl region at 1600-1800 cm^{-1} and hydroxyl region at 2750-3650 cm^{-1} were fixed by the Gaussian/Lorentzian peak shape. In previous study, the Gaussian/Lorentzian peak is applied for fitting peaks of degraded PET [34]. The others parameter of curve fitting were allowed to fit the observed spectra.

3.7.3 FT-Raman spectroscopy

A PET sample was placed on the tray, which is specifically designed for Raman characterization. The laser light from Raman spectrometer was focused on the sample. The focused point can be seen and adjusted through the camera that equipped with a computer. The PET specimen was subsequently collected by Raman spectrometer.

3.8 Preliminary study on the degradation of PET surface by UV irradiation

The primary assumption of UV evanescent field that can be induced surface degradation of PET was studied by UV irradiation coupled to homemade diamond μATR probe that attached with PET film sample at 1, 10, 30 minutes and characterized by FT-IR microscope spectrometer. In addition, the un-irradiated PET samples were irradiated at 1, 10, 30 minutes by conventional UV transmission, that is the same condition with the UV evanescent field irradiation. The results of irradiated PET spectra by conventional UV transmission were compared with that of the UV evanescent field irradiation.

3.9 Degradation of PET by UV irradiations

3.9.1 Degradation by the UV transmission technique

PET film samples were irradiated by UV transmission at 1-10 minutes and collected the infrared spectra by conventional ATR and diamond μATR. The results of irradiated PET spectra by conventional ATR were compared with that of novel diamond μATR. The peak changes at various times were plotted between the peak area against the hydroxyl region at 2750-3650 cm^{-1} (O-H stretching and –CH stretching) compared with the area of C=C aromatic skeletal at 1505 cm^{-1} due to the constant peak of aromatic skeletal without normalization process (unchanged peak under irradiation).

3.9.2 Degradation by the UV evanescent field technique

The irradiated PET film samples under UV evanescent field irradiation at 1-10 minutes were collected by diamond μATR that equipped with FT-IR microscope spectrometer. The peak changes at various times were plotted between the peak area against the hydroxyl region compared with the area of aromatic skeletal, that is the same as that of UV transmission irradiation.

3.10 Comparison of irradiated PET by both the UV evanescent field and UV transmission irradiations

Both irradiated PET film by transmission and evanescent field at 10 minutes were collected by ATR FT-IR spectroscopy and FT-Raman spectroscopy. The results were compared to those of un-irradiated PET. Moreover, spectra of the exposed side of the irradiated PET was collected and compared with those from the opposite side. The spectrum of irradiated PET by UV transmission was compared that of the annealed PET (i.e., a PET film was baked at 170 ℃ for 10 minutes). The peak changes of irradiated PET which were collected by ATR FT-IR spectroscopy were resolved by using curve fitting package of the OMNIC software. These results were evaluated and proposed the possible mechanism of photo-degraded PET.

3.11 UV evanescent field induced surface degradation of various PET

Various PET samples (staple fiber and filament) were irradiated under the UV evanescent field irradiation for 1-10 minutes. When the UV evanescent field irradiation was completed, the irradiated PET sample was immediately collected by ATR FT-IR spectroscopy without removing the sample.

3.12 Stability of hydrophilic species of irradiated PET under UV evanescent field

The irradiated PET films under UV evanescent field (1-10 minutes) were kept for three months at ambient condition. After three months, ATR FT-IR spectra of the irradiated PET samples were collected by the diamond μATR. These results indicate the stability of the hydrophilic species at the ambient condition.