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# Photodegradation of PEEK sheets under tensile stress

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## Abstract

The photochemical reaction of poly(ether ether ketone) (PEEK) sheets under tensile loads has been investigated. Two types of UV irradiation tests were carried out in a vacuum environment: with and without a cooling apparatus. Chemical structures, thermal properties, and mechanical properties were measured to clarify photo deterioration. Chemical analysis based on Fourier Transform Infrared Spectrometer (FT-IR) and X-ray Photoelectron Spectroscopy (XPS) showed photochemical scission caused by UV exposure. Thermal properties, measured by Differential Scanning Calorimeter (DSC), indicated that a crosslinking reaction occurred during the radiation tests. Tensile properties of PEEK sheets after UV radiation clearly showed a tendency to embrittlement affected not only by crosslinking but also by the orientation of molecular chains resulting from the temperature rise of the specimens. Furthermore, applied tensile stress during exposure accelerated molecular scission and disturbed the crosslinking effects of the tensile properties.

Key words: Photodegradation, Crosslinking, Polymer, PEEK, Space environment, Applying stress, Fourier Transform Infrared Spectrometer, X-ray Photoelectron Spectroscopy, Differential Scanning Calorimeter, Mechanical properties

## 1. Introduction

Photodegradation of polymeric material has been extensively investigated, and most studies of deterioration were generally conducted under UV irradiation [1-11]. Polymers are used under stress in most practical applications; therefore, several studies of the combined effect of photo-oxidation and mechanical stress have been discussed [12-16].

In recent years, high performance polymers have come into use in such real space environments as

structural materials, thermal blankets, solar cell paddles, etc [17-19]. Polymeric sheets are also essential for inflatable structures, which is state-of-the-art in the construction of space facilities [20-21]. There are many severe factors on polymers in low earth orbit (LEO) altitudes from 100 to 1000 km where the International Space Station (ISS) orbits. The main harsh factors of an LEO environment are high vacuum, thermal cycles, electron beam (EB) radiation, an atomic oxygen (AO) atmosphere, and ultraviolet ray (UV) radiation [17-19,22-26]. Especially, it is supposed that polymeric material used for structural elements or inflatable construction is degraded by UV radiation under stress applied in high vacuum environments. However, compared with those on ambient atmosphere, photodegradation studies of applied load in vacuums have scarcely been investigated.

This paper describes the photodegradation effect of poly(ether ether ketone) (PEEK) under tensile stress in the absence of oxygen. PEEK, a commercial polymer important for its high thermal stability and excellent formability, also has good resistance to such ionizing radiation as electron beams [22,27]. Previous photo deterioration studies of PEEK have mainly focused on chemical analyses [1,6,7,11]. In this paper, we concentrated on its mechanical properties. Besides, depending on the position in LEO, the temperature of the material rises to more than 100°C, which may affect the tensile properties of the PEEK sheets. To confirm the temperature effects, we conducted two types of experiments: UV exposure tests with and without a cooling apparatus. The specimens used in both tests were exposed by applying tensile loads in vacuum environments. Fourier Transform Infrared Spectrometer (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Differential Scanning Calorimeter (DSC), hardness tests, and tensile tests were applied to clarify the effects on photo deterioration under stress.

## 2. Experimental

### 2.1 Samples and irradiation tests

0.4 mm thick PEEK sheets (FS-1100C from Sumitomo Bakelite Co., Ltd.) were used. Fig. 1 shows the test pieces. Three types with different widths were fabricated from the sheet. The axial direction of each test piece was the same as the drawing direction of the sheet. Tensile loads were applied to the test pieces by deadweight during UV irradiation tests. The applied stresses of the tests were 0, 1.57 and 4.68 MPa.

Irradiation tests were carried out using the UV exposure device of the Japan Aerospace Exploration Agency (JAXA). The UV source (Yamashita Denso Co., Ltd.) was a 6 kW xenon lamp, and the wavelength range was 250 - 400 nm. Pressure in the test chamber was high vacuum on the order of  $10^{-5}$  Pa. The UV fluence was  $3.47 \times 10^4$  J/cm<sup>2</sup>, which is equivalent to about a half year of an ISS orbit. The temperature of the sample rose to about 130°C without a cooling apparatus. On the other hand, with cooling equipment during the test the maximum temperature was 80°C. Chemical

structure, thermal properties, and surface hardness were measured on the specimens of the exposure test without cooling apparatus. Tensile tests were conducted on the specimens of both exposure tests.

## 2.2 Measurements

The composition and chemical structure of the material surface were measured by FT-IR and XPS. IR spectra were recorded on a IR $\mu$ s-II FT-IR spectrophotometer (Spectratech Inc., nominal resolution of 4  $\text{cm}^{-1}$ , 128 scans summation). XPS analysis used ESCALAB 220i-XL (FI SURFACE SYSTEMS Inc.) with  $\text{AlK}_{\alpha}$  X-rays.

Thermal properties were measured by a DSC-6200 (Seiko Instruments Inc.) and were carried out in a  $\text{N}_2$  atmosphere at heating and cooling rates of 10°C/min. Heating ran to 400°C at which the material completely melted; cooling from 400°C was sequentially performed.

Hardness distribution on the cross-sectional areas of the specimens was measured by ENT-2100 (ELIONIX Co., Ltd.). The samples were cut after buried in resin. The bared cross sections were finished by buffing after polishing with emery paper from #400 to #1500. The applied load of the hardness test was set to 500  $\mu\text{N}$ . Measurements were done on 20 points from the UV exposure surface to the back with 20  $\mu\text{m}$  steps.

Tensile tests were carried out according to the ASTM D882-95a at a strain rate of 0.1/min. All tensile tests were conducted in a room held at a temperature of 23 $\pm$ 2°C and a relative humidity of 50 $\pm$ 5%. Tensile specimens were cut out from the test piece of Fig. 1 to the widths of 1mm using a razor blade. Namely the size of the tensile specimen was 0.4mm  $\times$  1mm  $\times$  97mm. Before the tensile tests, these specimens had been conditioned for 48 hours at a temperature of 23 $\pm$ 2°C and a relative humidity of 50 $\pm$ 5%.

## 3. Results

### 3.1 Chemical analysis

UV irradiation changed the IR spectra of the samples. The IR spectra of the pristine sample and the UV exposed sample are shown in Fig. 2. Changes occurred in mainly three zones of the IR spectra: hydroxyl, carbonyl, and complex. After UV irradiation, an increase of absorbance was observed in a range from 3150 to 3700  $\text{cm}^{-1}$ , showing a maximum value around 3400  $\text{cm}^{-1}$ . The maximum is in the range of polymeric hydrogen-bonded OH stretch [1,29]. In the carbonyl region, an increase of absorbance around 1730  $\text{cm}^{-1}$  was recorded. This hump, which fits the ester band of the O-C=O, indicates the phototransformation of benzophenone units [1,29]. In the complex region, a decrease in absorbance was observed at around 1215  $\text{cm}^{-1}$ . Since the absorbance corresponds to the aromatic ether structure, the decrease suggests a reduction of the ether bond. There were no significant differences between the IR spectra of the specimen irradiated under no tension and under

4.68 MPa.

The XPS C1s spectrum of the pristine sample and the UV exposed sample are shown in Fig. 3. At around 286.0 and 288.5 eV, there were differences between the pristine (Fig. 3(a)) and the UV exposed sample (Fig. 3(b)). Table 1 summarizes the XPS peak deconvolution results. The peak at 286.0 eV decreased, and the peak at 288.5 eV increased after UV exposure. The peak at 286.0 eV comes from ether structure and at 288.5 eV from O-C=O. The FT-IR and XPS results suggest that UV reacts to the aromatic ether bond, which is the weakest bond in the polymer structure, and forms OH and O-C=O.

### 3.2 Thermal properties

The DSC results and the thermal parameters after UV exposure are shown in Fig. 4 and Table 2 respectively. Irradiated specimens showed a higher glass transition temperature ( $T_g$ ) than the pristine specimens, regardless of stress. The heat of crystallization ( $\Delta H_c$ ) of the exposed sample clearly decreased compared to the pristine sample.  $\Delta H_c$  after exposure was almost the same regardless of applied stress. Furthermore, the melting temperature ( $T_m$ ) and heat of melting ( $\Delta H_m$ ) decreased after UV radiation.

### 3.3 Hardness

Fig. 5 shows the hardness on the cross-sectional areas of the specimen, which was higher after exposure than the pristine sample at depths from 0 to 250  $\mu\text{m}$ . However, this tendency could not be seen in the deeper regions from 250 to 400  $\mu\text{m}$ . Namely, PEEK surface was hardened by UV radiation, and the UV penetration depth was about half the thickness of the test piece.

### 3.4 Tensile properties

Fig. 6 shows the stress-strain curve of the pristine PEEK and the UV exposed sample whose temperature rose to 130°C during the test. The stress-strain curve of the pristine sample exhibited ductile behavior. On the other hand, the irradiated specimen showed a different tendency: higher yield strength and lower elongation at the break. This tendency could also be seen in the stress-strain curve of the sample exposed to the cooling apparatus. More details of the yield strengths and elongations are shown in Fig. 7. Fig. 7(a) indicates that the yield strengths of the UV exposed samples were higher than the pristine samples. Fig. 7(b) shows that the elongations of the UV exposed samples were much lower than the pristine samples. The exposed sample elongations decreased with increasing applied stress.

Yield strengths and elongations after UV radiation tests with a cooling apparatus are shown in Fig. 8. Fig. 8(a) indicates that the yield strengths of the irradiated samples under no tension were higher than the pristine samples. On the other hand, the yield strengths of samples exposed under tension

were lower than those under no tension. Fig. 8(b) shows significantly lower elongations of exposed samples than the pristine. The elongations of samples irradiated under tension were slightly lower than those of no tension.

Although there were differences in the detailed tendencies of the tensile properties after the two types of exposure tests, the PEEK sheet was clearly embrittled by UV radiation.

#### 4. Discussion

Chemical analysis based on FT-IR and XPS showed the occurrence of phototransformation as well as photodissociation. A previous study reported that aromatic ethers are dissociated from main molecular chains and subsequently recombined to esters by UV radiation [1]. For UV exposure to aromatic polymers, crosslinking reactions are caused in parallel to chain scission [1-2,10]. The main chain scissions occur as consequences of primary photodissociation and secondary radical formation [5]. If free radicals migrate, they can recombine with other radicals and then produce crosslinking [1,2,5]. According to these studies, our chemical analysis results indicate that UV radiation causes both chain scission and crosslinking.

The influences of crosslinking could definitely be seen in the results of thermal properties after UV irradiation. The  $T_g$  of the exposed samples shifted to higher temperatures.  $\Delta H_c$ ,  $T_m$ , and  $\Delta H_m$  decreased after UV exposure. Similar aromatic polymer results regarding the change of thermal parameters caused by ion or UV irradiation have been reported [4,11,27,28]. The increase of  $T_g$  and the decrease of  $\Delta H_c$  are caused by crosslinking reactions during radiation [4,27,28]. Based on the thermal parameters of previous studies and our tests, UV exposure clearly causes crosslinking.

In general, crosslinking results in the embrittlement of polymeric material [4,27]. In our study, the PEEK surface was hardened by radiation. The depth affected by UV was about half of the specimen thickness. Besides, tensile properties of PEEK after UV showed increases of yield strengths and decreases of elongations, indicating that the depth of UV penetration is sufficient to affect tensile properties and that the embrittlement of PEEK is caused by crosslinking resulting from UV exposure.

As shown in the tensile test results whose samples were exposed to a cooling apparatus, yield strengths irradiated under stress were lower than those with no tension (Fig. 8(a)). Although our tests were conducted in a vacuum, similar results were obtained in an ambient atmosphere. Previous studies showed that tensile stress accelerates molecular scission during photo-oxidation [12-14,30]. Scission accelerated and dominated crosslinking [14]. Therefore, the effect of crosslinking on yield strengths is disturbed by scission acceleration resulting from applying stress. On the other hand, the yield strengths of specimens whose temperature rose to 130°C during UV exposure increased with increasing applied stress (Fig. 7(a)). This result may be caused by molecular orientation due to high

temperatures and tensile stress, suggesting that applying stress can differently affect the mechanical properties of polymers exposed to UV because of their temperature.

It is evident from the results and discussion presented here that PEEK is embrittled by crosslinking that results from UV exposure and that the mechanical properties of PEEK can be affected by applied tensile stress and temperature during irradiation. This should be considered when designing structures used in actual space environments.

## 5. Conclusion

The photodegradation of PEEK under tensile stress equivalent to an LEO environment was investigated using FT-IR, XPS, DSC, and hardness and tensile tests. The results confirmed that both crosslinking and molecular scission are caused by UV radiation. The tensile properties of PEEK sheets after exposure indicate a tendency to embrittlement caused by crosslinking. Besides, applying tensile stress accelerates molecular scission during UV exposure, inhibiting the crosslinking effect on the tensile properties. On the other hand, the orientation of molecular chains, which can be induced by the interaction between applied tensile stress and high temperature, affects tensile properties.

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Figures Captions.

Fig. 1. Test pieces.

Fig. 2. FT-IR spectra of PEEK sheets. (a): Pristine sample, (b): UV exposed sample under 4.68 MPa.

Fig. 3. XPS C1s spectrum of PEEK. (a): Pristine sample, (b): UV exposed sample under no tension.

Fig. 4. DSC traces of pristine and UV exposed specimens.

Fig. 5. Hardness of pristine and UV exposed samples under no tension.

Fig. 6. Stress-strain curves of pristine and UV exposed specimens.

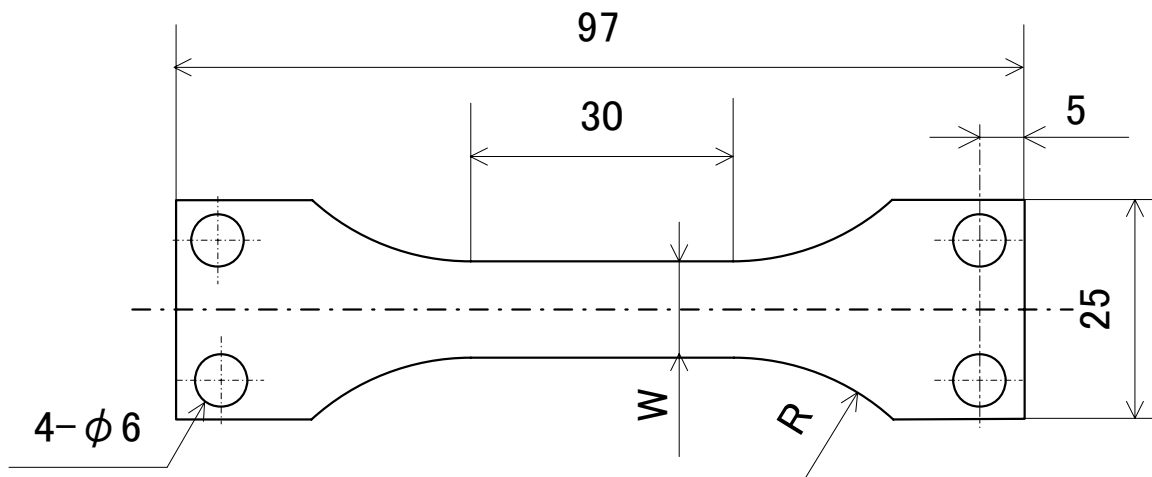
Fig. 7. Tensile properties of pristine and exposed samples without cooling apparatus. (a): Yield strength, (b): Elongation at break.

Fig. 8. Tensile properties of pristine and exposed samples with cooling apparatus. (a): Yield strength, (b): Elongation at break.

Table Caption.

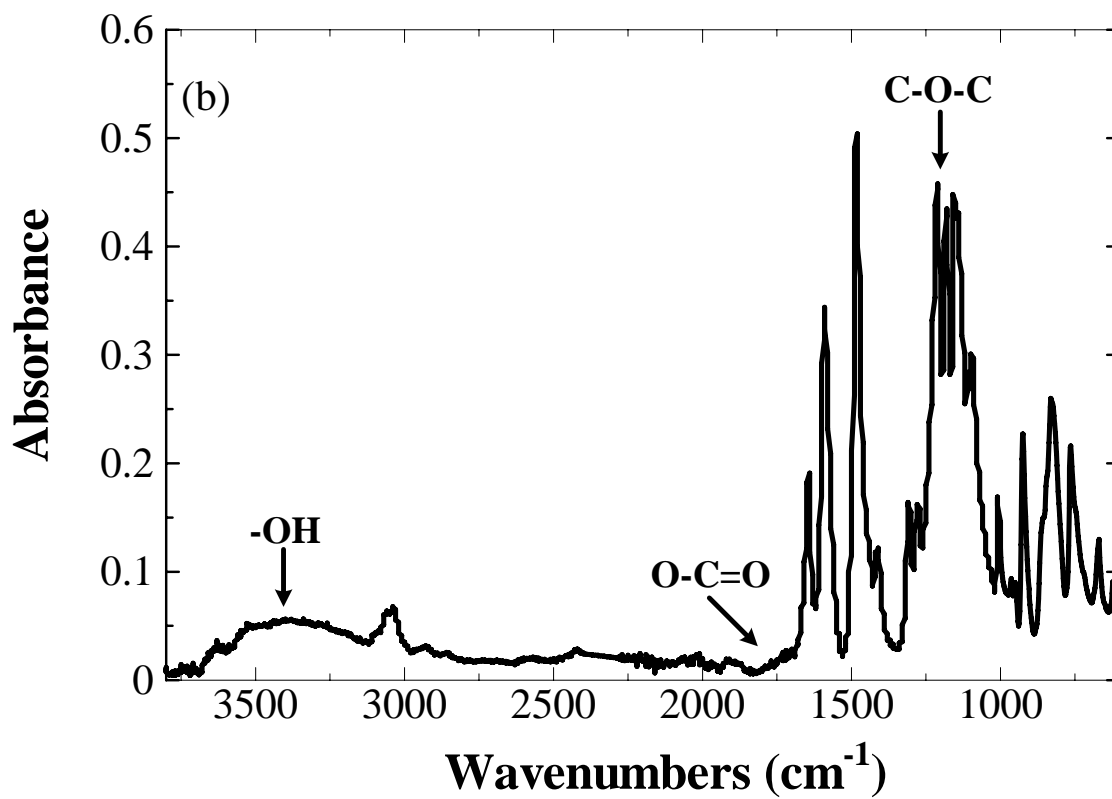
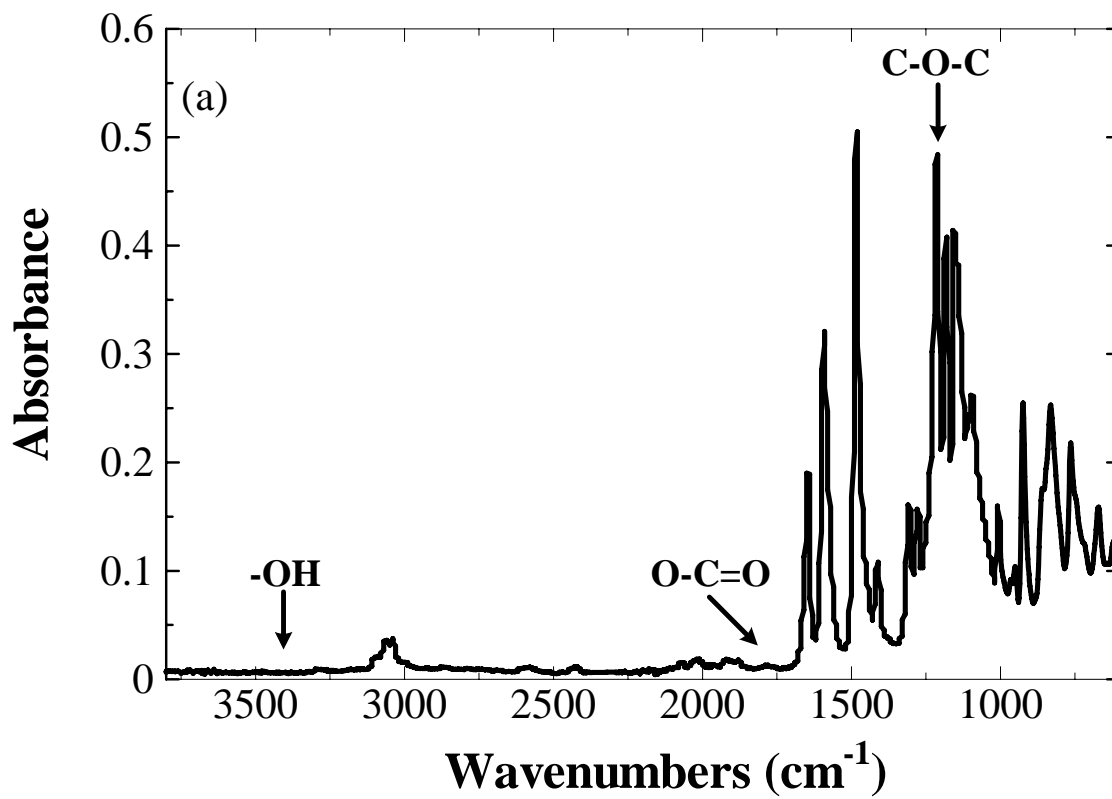
Table 1. Summary of XPS peak deconvolution results.

Table 2. Thermal parameters of pristine and UV exposed specimens.

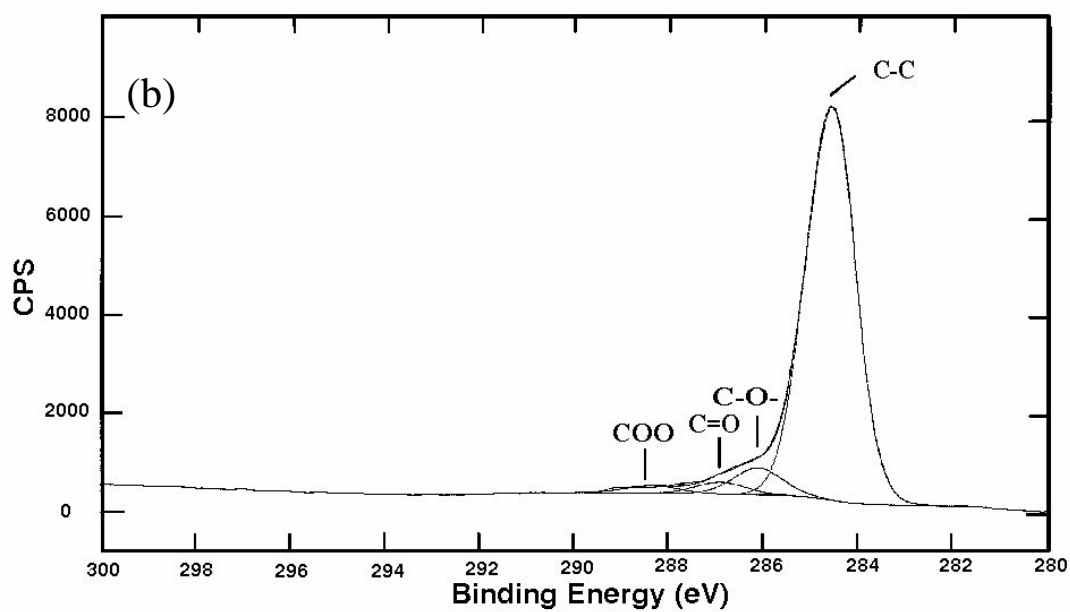
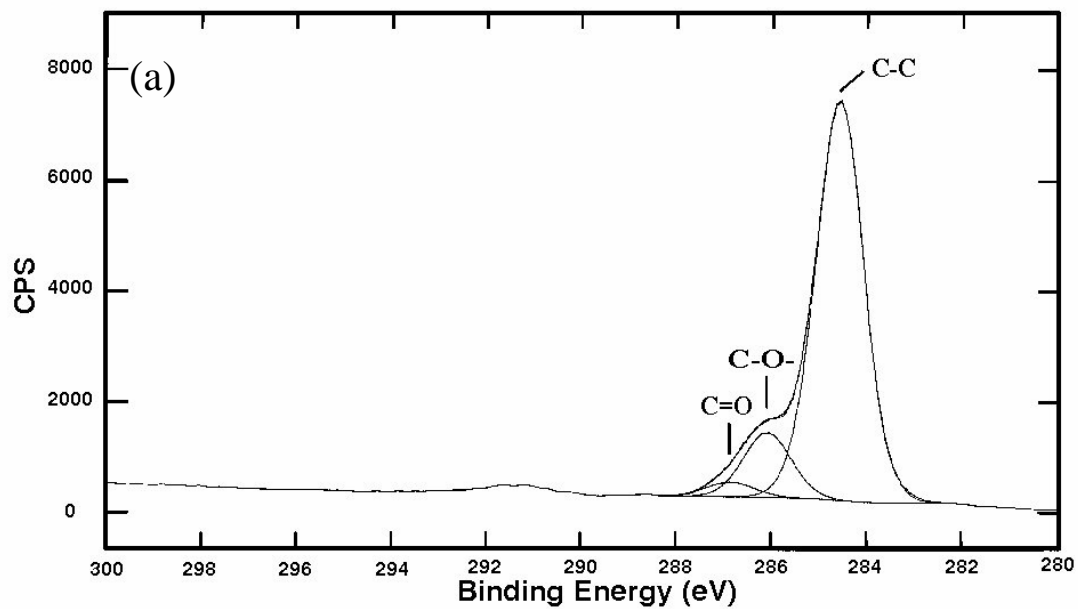


W (mm)	R (mm)	Tensile load (N)	Tensile stress (MPa)
25	-	0	0
7.8	21	4.90	1.57
11	27	20.6	4.68

Figure 1.



Figures 2.



Figures 3.

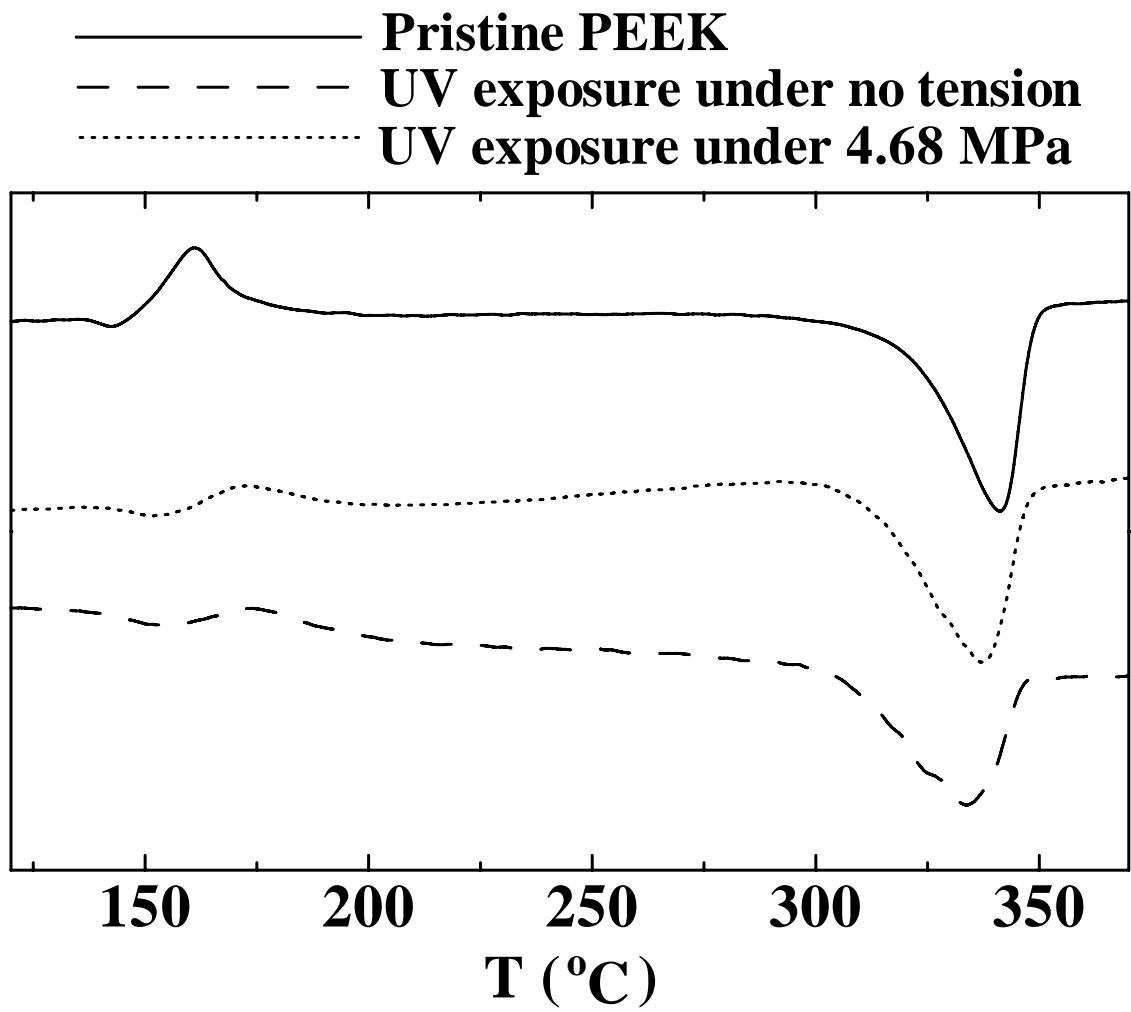


Figure 4.

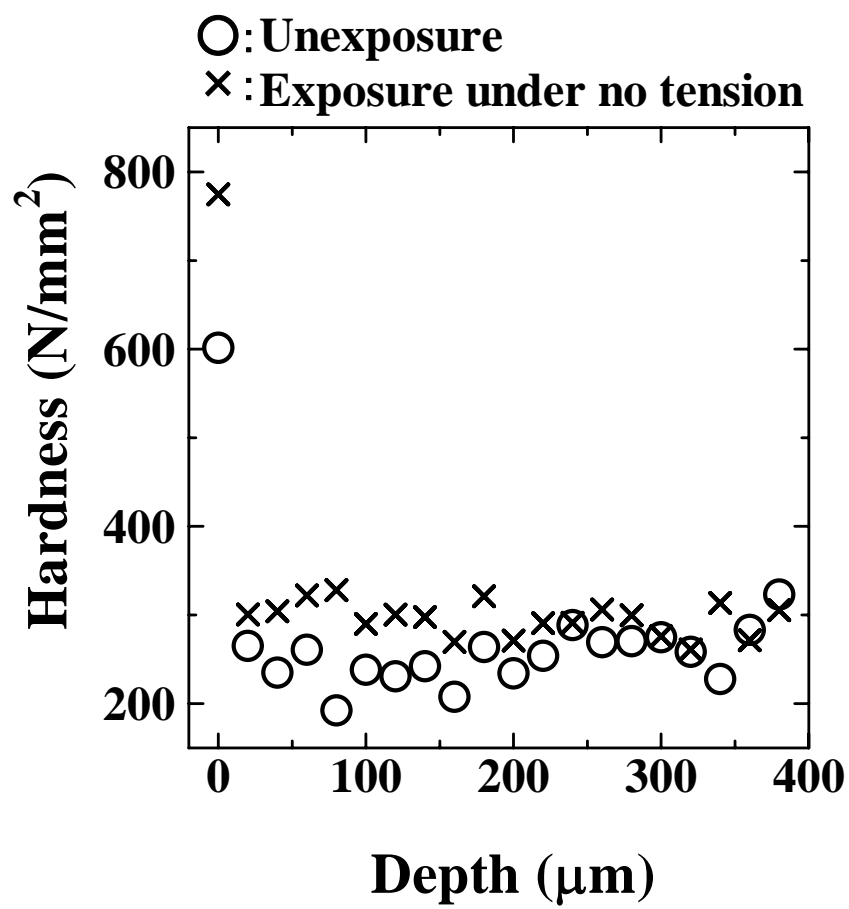


Figure 5.

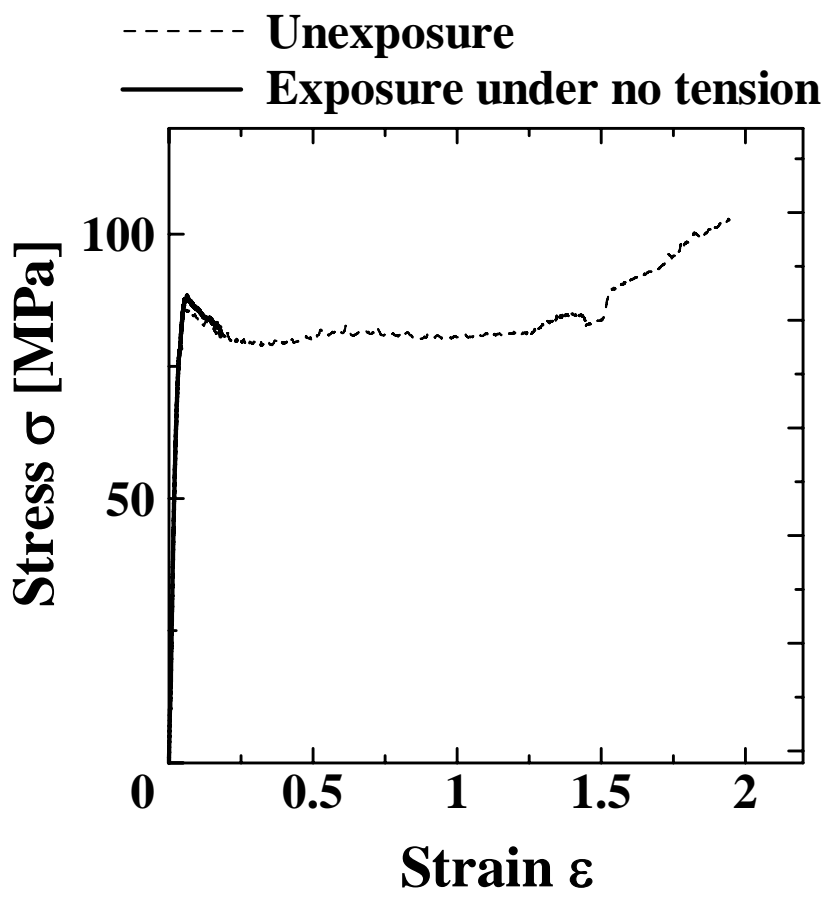
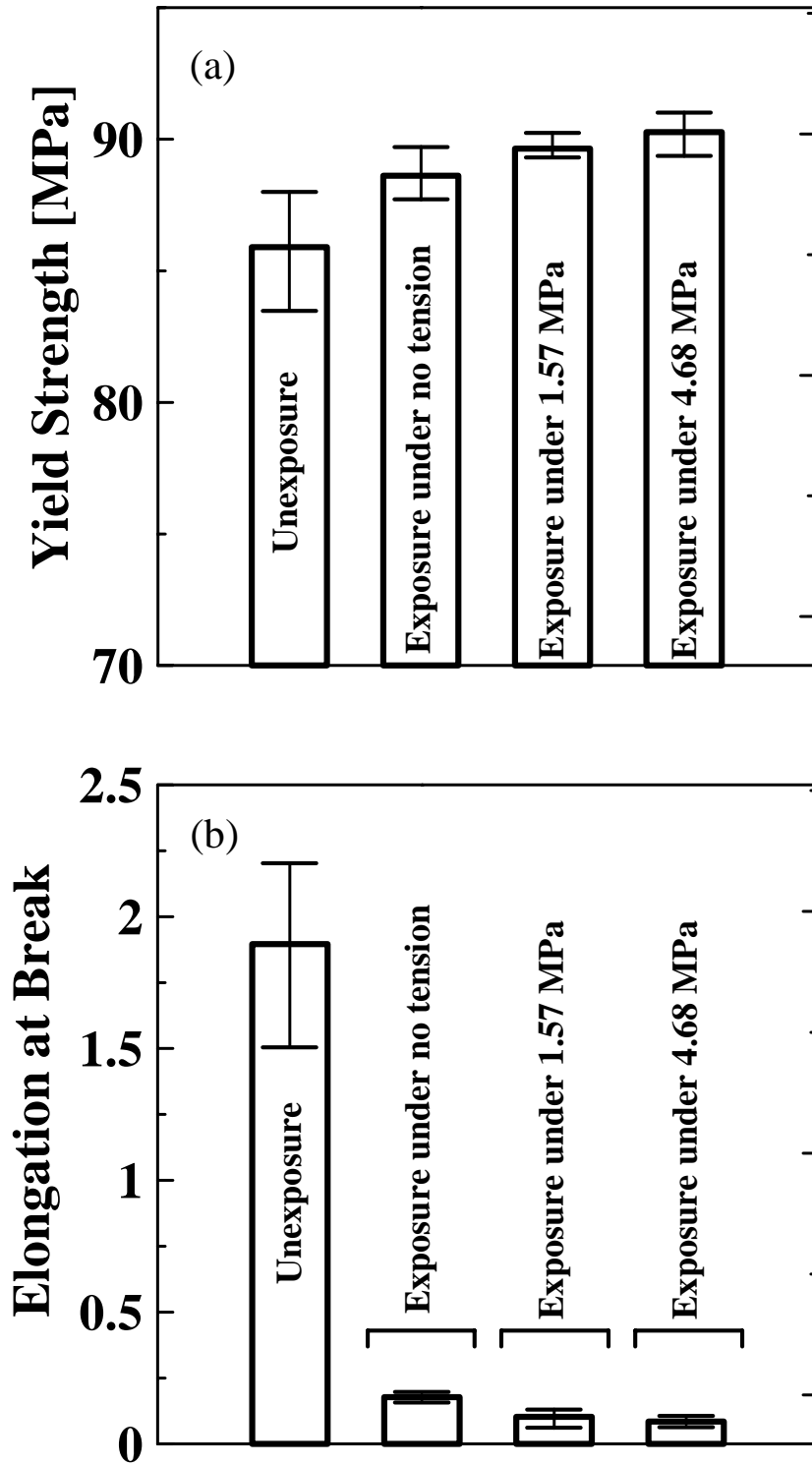
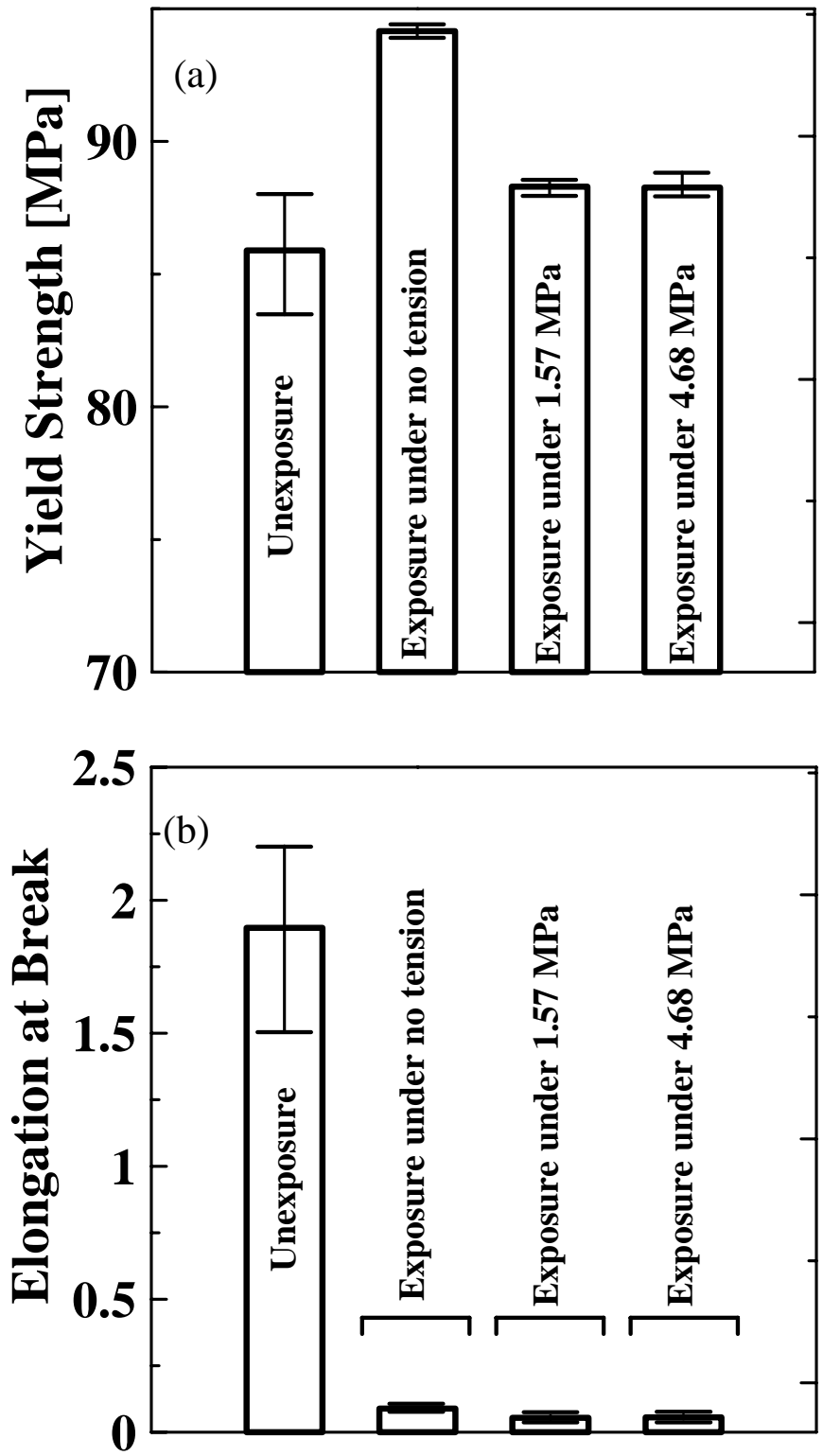


Figure 6.



Figures 7.



Figures 8.

Table 1.

	C type (%)			
	C-C	C-O	C=O	COO
Binding energy (eV)	284.6	286.0	287.0	288.5
Pristine sample	83.6	13.5	2.9	-
UV exposed sample under no tension	89.5	6.1	2.7	1.7

Table 2.

	$T_g$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
Pristine PEEK	142.3	14.5	340.5	45.3
UV exposure under no tension	153.1	6.08	333.7	33.8
UV exposure under 4.68[MPa]	151.5	6.28	337.0	37.6