DOI 10.1007/s11595-014-1080-7

Effect of Accelerated Xenon Lamp Aging on the Mechanical Properties and Structure of Thermoplastic Polyurethane for Stratospheric Airship Envelope

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Abstract: This study aimed to investigate the effect of artificial weathering test on the photoaging behavior of TPU films. Changes in mechanical properties, morphology and chemical structures are studied by tensile test, scanning electron microscopy, atomic force microscopy, Fourier-transformed infrared, and X-ray photoelectron spectroscopy. The results show that the photoaging negatively affects the initial modulus and stress at break values of TPU films. The surface of the specimen that is exposed to irradiation becomes rough, and some visible micro-defects such as blisters and voids can be detected. The morphology of the fracture surfaces illustrates that irradiation reduces the plasticity but increases the brittleness of the TPU films. The chemical structure analyses of the accelerated aged films prove that chemical structural changes in TPU films occur. The irradiation may break the long molecular chains on the surface of the specimens and form the low-molecular weight oxygen-containing groups. The number of chain scissions increases with the increase in exposure time.

Key words: thermoplastic polyurethane; envelope; xenon lamp; aging

1 Introduction

In recent years, increased interests have focused on the stratospheric airships, which can be used to capture and transmit information efficiently[1,2]. However, the characteristics of stratospheric environment[1,3] pose significant challenges on airship envelope materials. To adapt to the working environment in the stratosphere, the surface materials of an envelope must resist the harsh stratospheric environment such as intense ultraviolet (UV) radiation[1,3]. Therefore, studying the weatherability of the weather-resistant layer materials of airship envelope is necessary.

Thermoplastic polyurethane (TPU) films are versatile polymeric materials, which can be used for weather-resistant layer materials in the design of envelope materials[1]. However, TPU films, like other polymeric materials, are also susceptible to changes in structure and chemical composition when exposed to aggressive environments (*e g*, UV radiation)[4-6], which deteriorate the significant properties of TPU films. In the last few years, the influence of the aging process on the lifetime of polymer has attracted increasing attention. Several studies on the effect of natural aging on mechanical and other properties of polyurethane materials have been reported. Oprea *et al*[7] studied the mechanical behavior of polyurethane films using natural weathering tests under different aging conditions. However, natural weathering tests are usually time consuming and their reproducibility is not efficient; therefore, artificial accelerated weathering tests are widely used to simulate natural weathering conditions.

Previous studies have also reported that xenon, UV, and carbon-arc lamps are commonly used as light sources to simulate UV radiation from the sun[8,9]. Such artificial accelerated aging has been demonstrated in several studies on the aging characteristics of TPU

(Received: Dec. 25, 2013; Accepted: Mar. 20, 2014)

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Funded by the Fundamental Research Funds for the Central Universities (No.HIT.KISTP.201408)

material exposed to UV lamp environment as well as carbon-arc lamp exposure[10,11]. However, studies on the aging behavior of TPU films upon exposure to xenon lamp weathering environment have not been fully described. Xenon lamp produces a broad spectrum similar to natural sunlight; however, it exhibits higher relative intensity at short wavelengths[12], which can simulate the harsh environment of the stratosphere more accurately. To prevent TPU films from photoaging and restrict the degradation of performance, studying the law of influence of photoaging on the mechanical properties and structure of TPU films is necessary if the suitability of TPU film for long service life applications in aggressive environments is required. In this paper, the artificial weathering test was performed under the xenon lamp accelerated aging condition. The mechanical properties were determined using an electron-mechanical universal material testing machine. Surface morphologies of the films were examined through atomic force microscopy (AFM) and scanning electron microscopy (SEM). The surface degradation behavior was evaluated with Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

2 Experimental

2.1 Materials

The TPU films (Type 1003) used in this study were purchased commercially, which were made by Jin Heung Environmental Protection Material Co., Ltd. The principal characteristics of the TPU films are listed in Table 1.

Table 1 Principal characteristics of the studied TPU films

Property	Value
Thickness/μm	100
Density/(g/m^2)	120
Maximum temperature service/℃	>350
Breaking strength/MPa	⩾80
Initial modulus/MPa	⩾50
Breaking elongation/%	⩾490

2.2 Artificial weathering test

The artificial weathering test was performed according to AATCC 16E to evaluate the durability of the studied TPU films. Atlas Ci3000+ xenon arc weather-ometer was used, which simulated the severe conditions for climatic aging. The light source used was a 4500 W water-cooled xenon lamp, which provided radiation at wavelengths of 300-400 nm. The specimens were exposed to the combined effects of radiation, temperature, and wind at different time intervals up to 480 h. After the samples were exposed to radiation, they were taken out to investigate the mechanical properties, surface morphology, and chemical composition.

2.3 Characterization methods

To study the effect of irradiation on the mechanical properties of TPU, uniaxial tensile tests were conducted using an electromechanical universal material testing machine (Instron 5500R, USA). This machine was equipped with a measuring load cell at a crosshead velocity of 300 mm/min and a gauge length of 180 mm at 20 ± 2 ℃.

The morphologies of the film surface (before and after irradiation) were examined under a Quanta 200 FEG scanning electron microscope. Prior to viewing, the samples were gold coated according to the standard technique. The acceleration voltage was 30 kV. Images of each specimen were collected at 100× to 10 000× magnifications. The surface topography of the specimens (before and after irradiation) was further characterized by atomic force microscope (NT-MDT P47, Russia). Topography images were recorded for each TPU film on various scanned areas. The average surface roughness (R_a) was directly calculated from the AFM images.

FT-IR spectroscopic analysis was performed on a Nicolet Nexus 670 FT-IR spectrometer to assess the structural degradation of the specimens. The films were mounted on a Nicolet OMNI-Sampler at a constant pressure with a grip. To obtain the spectrum, 24 scans were collected at a resolution of 2 cm^{-1}.

XPS analysis was performed on a K-Alpha model spectrometer using a focused (diameter of the irradiated area was 400 μm) monochromatic Al Kα radiation (12 kV; 6 mA). The binding energy (BE) scale was fixed at 285.0 eV to the C1s peak. The data were examined using the XPS peak software for spectra deconvolution and curve fitting.

3 Results and discussion

3.1 Mechanical properties analysis

The change in mechanical property with aging time is used as the main index to determine whether the material is aging. Accordingly, tensile tests of the TPU films were conducted to identify the factors that cause the changes in mechanical property. Each tensile value of the TPU film represents the average

of three experiments. The stress at break values for the films without accelerated aging and the films that were exposed to irradiation with xenon lamp for 48, 120, 240, 360, and 480 h are shown in Fig.1. The stress at break values of TPU films significantly decreases as irradiation is prolonged. However, the decrease in stress at break becomes moderate when the aging continues for a longer period. The loss of mechanical performance is 49.27% for the longest radiation exposure time.

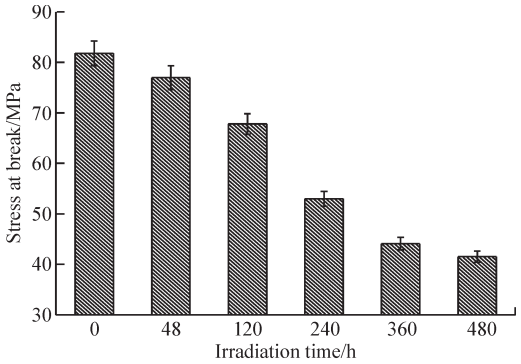

Fig.1 Variation in stress at break versus the xenon lamp irradiation time

Based on the uniaxial tensile test and the concept of stress and strain, the Young's modulus of TPU films can be expressed as follows:

$$E = \frac{\Delta P / bd}{\Delta l / l_0} \tag{1}$$

where, ΔP is the initial load, Δl is the displacement of the specimen during the tensile test, and l_0 is the initial distance of the two fixtures. b and d represent the width and thickness of the specimen, respectively. The values of the initial elastic modulus obtained from Eq.(1) for unaged and aged specimens are shown in Fig.2. The initial elastic modulus of TPU films increases when the films are exposed to xenon lamp irradiation, which indicates that the specimens increasingly become stiff.

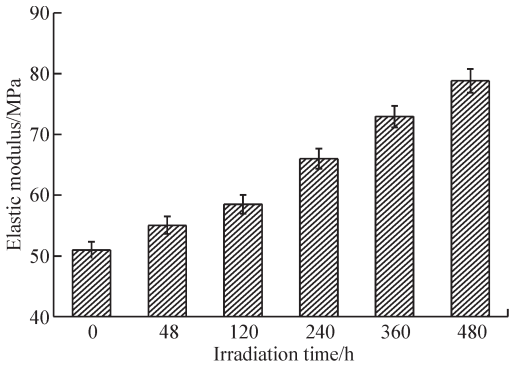

Fig.2 Variation in initial elastic modulus versus the xenon lamp irradiation time

The initial modulus reaches 78.82 MPa for the longest radiation exposure time.

During photoaging, the loss of volatile matter (water molecules, plasticizer) may negatively affect the initial modulus and stress at break values of TPU films. The generalized oxidization reaction and chain scission process likely result in the loss of mechanical properties.

3.2 Surface morphology characterization

To further explore the effect of photoaging on the surface of TPU films, SEM was performed. Figs.3(a) and 3(b) show the SEM surface morphology of unaged and aged TPU films, respectively. The surface of the unaged specimen is relatively smooth. However, the surface of the specimen that is exposed to irradiation for 480 h becomes rough, and some visible micro-defects such as blisters and voids can be detected, which indicate that the artificial weathering process can make the film surface rougher. SEM images of fractured surface from the tensile tests of unaged and aged TPU are shown in Figs.3(c) and 3(d), respectively. The fracture surface of the unaged specimen is relatively ductile. The fracture surface of aged TPU films at 480 h shows a significant change in the fracture topography; particularly the broad fracture path is accompanied by several tear lines. Thus, irradiation changes the TPU film from a ductile form to a brittle one. The excessive embrittlement likely results in the formation of micro-cracks. Therefore, irradiation causes severe damage on the surface of the specimens. The SEM images of the fracture surfaces also illustrate that irradiation reduces the plasticity but increases the brittleness of the TPU films, which are in agreement with the results of the mechanical properties.

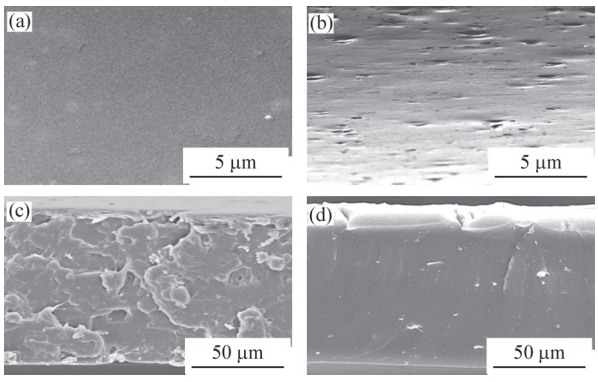

Fig.3 SEM images of TPU films: (a) surface of unaged film; (b) surface of aged film for 480 h; (c) fracture surface from the tensile test of unaged film; and (d) fracture surface from the tensile test of aged film for 480 h

Fig.4 shows the three-dimensional (3D) AFM images of unaged and aged TPU films. To quantify the

effects of the irradiation, the surface R_a of each film is calculated directly from the AFM images (Table 2). The presented results are the average of three measurements for each sample and determined within a 700 μm × 700 μm surface region. AFM images were taken 2 h after irradiation on the surface of the specimens without contacting any water. Fig.4(d) shows many straight pillars with different heights. These pillars likely correspond to the low-molecular weight oxidized species[13], which form on the surface of specimens when treated with irradiation. An increasing number of low-molecular-weight oxidized species are produced on the surface as the duration of aging is increased, thereby gradually increasing R_a on the treated surface of TPU films. Table 2 shows that the R_a of TPU films also increases as the irradiation time is increased, which is in agreement with the AFM images in Fig.4.

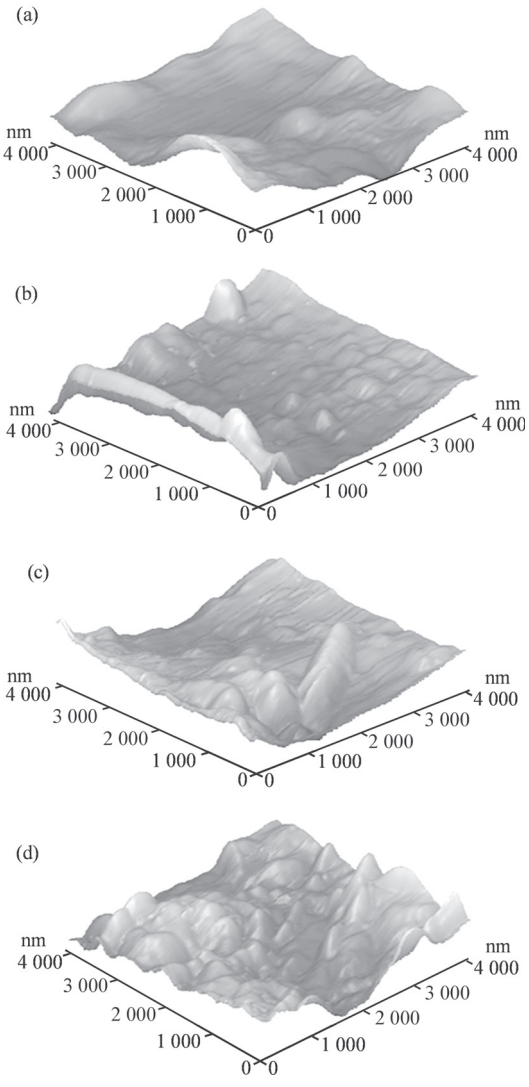

Fig.4 3D AFM topographic images of TPU films for different irradiation times: (a) 0 h; (b) 120 h; (c)240 h; and (d) 480 h

Table 2 Average surface roughness R_a of unaged and aged TPU films

Irradiation time/h	R_a/nm
0	7.717
48	8.911
120	9.969
240	10.813
360	12.429
480	17.012

3.3 FT-IR spectroscopy analysis

Table 3 Infrared characteristic frequencies of TPU films

Frequency/cm^{-1}	Relative intensity	Main assignment
3 334	s	ν(N-H)[15]
2 948, 2 867	s, w	$\nu(CH_2)$[16]
1 732-1 702	vs	ν(C=O)[5,16]
1 528	s	ν(C-N)[6]
1 361	vw	$\omega(CH_2)$[17]
1 306	w	ν(C-N-C)[18]
1 218, 1 175, 1 138	vs, w, w	ν(C-O-C)[6]
1 067, 1 014	s, w	ν(C-O-C)[6, 17]

Note: The relative intensity is based on the whole infrared spectrum of a sample at room temperature: s = strong, w = weak, vs = very strong, vw = very weak, ν = stretching vibration, ω = wagging vibration

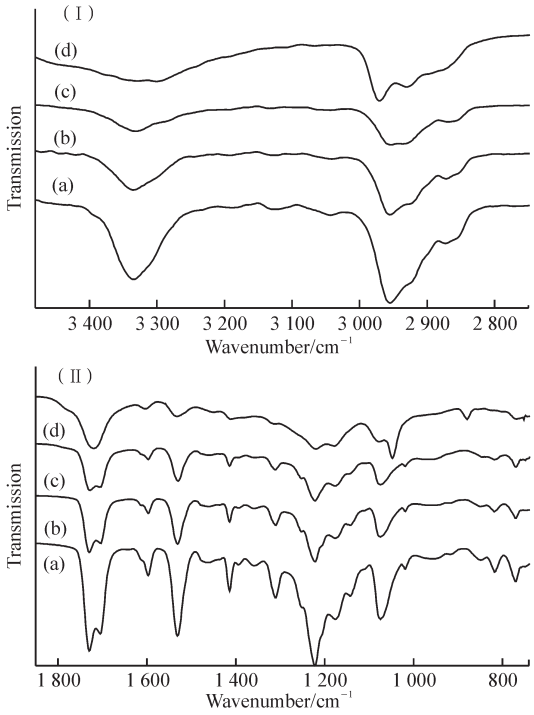

Fig.5 FT-IR spectra of TPU films for different irradiation times: (a) 0 h; (b) 120 h; (c) 240 h; and (d) 480 h

FT-IR experiments were performed using the samples before and after accelerated aging for 120, 240, and 480 h, respectively. The FT-IR spectra of different aged samples exhibit significant changes in the structure of the material (Fig.5). The most distinct IR bands of the unaged TPU films are summarized in

Table 3. No shift of the peaks is found in the FT-IR spectrum (Fig.5). The spectra of the aged TPU films do not show any indication of newly formed groups compared with that of the unaged TPU film, although a decrease in the intensity of N-H and C-H bands for irradiated samples may be observed. In particular, the C-N-C band almost disappeared after the sample was irradiated for 480 h. To further analyze the changes in various groups at different irradiation times, the peaks are normalized using the peak areas, which is likely to be a more reliable method than using the peak intensity[14].

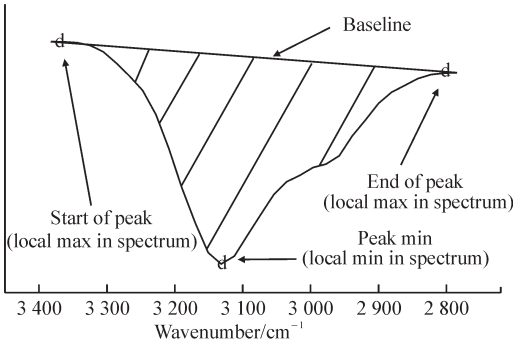

Fig.6 Schematic of the peak area determination

Table 4 Changes in the peak area ratios for different irradiation times

Characteristic peak	0 h	120 h	240 h	480 h
N-H (3334 cm^{-1})	5.0489	4.0256	2.4902	1.5667
C-H (2948, 2867 cm^{-1})	3.3619	2.2183	1.9543	1.4775
C=O (1732, 1702 cm^{-1})	8.4524	8.8201	10.7452	19.6604
C-N (1528 cm^{-1})	4.3136	4.3057	4.0535	3.6255
C-H (1361 cm^{-1})	0.2043	0.1964	0.1834	0.1119
C-N-C (1306 cm^{-1})	1.1624	1.0132	0.7860	0.0031
C-O-C (1218-1014 cm^{-1})	17.0438	18.0176	19.5577	25.9996

For spectral peak area analysis, selecting the reference peak that remains unaffected throughout the whole aging treatment is preferred to reduce the quantitative error. The peak located at approximately 1 594 cm^{-1}, which is attributed to the benzene ring skeleton, is selected as the reference band. The integral method is used to calculate the peak area, and the peak area is the integral area of the spectral line to the baseline (Fig.6). Each calculated peak area is divided by the selected reference peak area in each spectrum; thus, the peak area ratio is obtained. Table 4 lists the changes in the peak area ratios of all of the characteristic peaks at different irradiation times. The gradual increase in the peak area ratios of a certain functional group indicates that the amount of this functional group increases. By contrast, a gradual decrease suggests that the amount of the functional group decreases. The fractures of a given bond occur, which becomes more serious as the irradiation time is increased, when the irradiation energy of xenon lamp exceeds a specific BE. As shown in Table 4, the peak area ratios of the bands at 3 334, 2 948, and 2 867 cm^{-1} (stretching vibrations of N-H and C-H), 1 528 cm^{-1} (stretching vibration of C-N), 1 361 cm^{-1} (wagging vibration of C-H), as well as 1 306 cm^{-1} (stretching vibration of C-N-C) decrease with the increase in the duration of aging, indicating that the bonds may break during the process of accelerated aging. The increase in the peak area ratios of some bonds also occur, such as the stretching vibration of carbonyl bond in ester at 1 732 and 1 702 cm^{-1}, as well as the symmetric stretching vibration of C-O-C bond at 1 218, 1 067, and 1 014 cm^{-1}.

Thus, longer irradiation time can easily break a single bond and produce more oxygen-containing groups. Considering the previous mechanical and surface morphology analysis, xenon lamp irradiation can lead to the destruction of the original structure, which results in the decrease in the mechanical properties of the TPU films. To understand further, XPS measurements from the unaged and aged samples were performed.

3.4 XPS analysis of chemical surface changes

A low-resolution scan was run to determine the percentages of the elements present at the surface and evaluate the weathering performance of the TPU surfaces (before and after irradiation by xenon lamp at different times). Table 5 shows the change in the elemental composition. The atomic ratios of carbon to oxygen (C/O) and oxygen to nitrogen (O/N) are obtained from the XPS spectra as an initial indication of surface oxidation. Table 5 also reveals that the changes are observed with the surface atom composition of TPU after irradiation, and oxygen percentage considerably increases after aging, which indicates that the surface is oxidized after xenon lamp irradiation.

Table 5 Surface elemental composition determined from XPS analysis

Irradiation time/h	Atomic percentage/%			Atomic ratio	
	C1s	O1s	N1s	C1s / O1s	O1s / N1s
0	88.63	7.03	4.34	12.61	1.62
48	87.05	8.85	4.10	9.84	2.16
120	85.13	10.79	4.09	7.89	2.64
240	84.30	12.14	3.57	6.94	3.40
360	72.33	23.86	3.81	3.03	6.26
480	69.27	26.48	4.25	2.62	6.23

A high-resolution scan was conducted on the C1s region for TPU films to characterize quantitatively

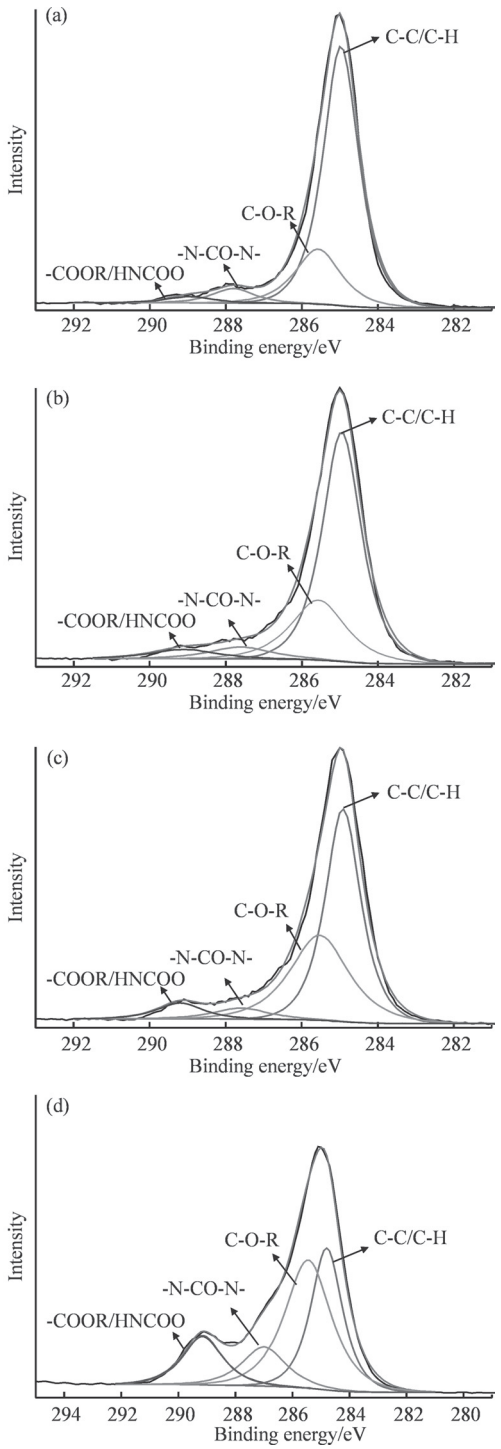

Fig.7 C1s XPS spectra of TPU films for different irradiation times: (a) 0 h; (b) 120 h; (c) 240 h; and (d) 480 h

Table 6 Relative composition ratio based on the area of each peak in the C1s spectrum fitting curve of pristine and aged TPU films

Irradiation time/h	0	120	240	480
C-C/C-H	73.2 %	65.9 %	51.7 %	31.9 %
C-O-R	19.8 %	24.3 %	34.7 %	42.1 %
-N-CO-N-	4.7 %	5.4 %	7.4 %	12.2 %
HNCOO/-COOR	2.5 %	4.4 %	6.2 %	13.8 %

the change in the concentrations of various functional groups, determine the types and amounts of present chemical bonds, as well as identify the chemical structure changes that occur. For a detailed chemical analysis in the C1s spectrum of each TPU film, the characteristic peaks that correspond to C1s are detected by a curve-fitting method (Fig.7). The quantitative characteristics of the correlative functional groups on the surface of each TPU film are shown in Table 6. The peak corresponds to C-C or C-H bonding centers at 285.0 eV (reference used to correct for the charge accumulation). The peak at 285.4 eV corresponds to the ether (C-O-C) group, where the carbon atom is single-bonded to the oxygen atom. The peak at 285.4 eV can also be attributed to C-O and C-N single bonds. The third peak located at 287.8 eV corresponds to the urea group (-N-CO-N-). The last peak located at approximately 288.9 eV corresponds to the urethane group (N-COO), and this peak can also appear due to the presence of -COOH group. As shown in Table 6 and Fig.7, C-C bonding is dominant on the surface of the unaged TPU film. A significant decrease in the area ratio after irradiation treatment indicates that the amount of C-C bonding is decreased, *i e*, the percentage of unoxidized carbon atoms is decreased. By contrast, the amount of oxygen increases with prolonged xenon lamp irradiation, which is indicated in the increasing amount of C-O-R, -N-CO-N-, and HNCOO groups. Thus, the oxygen from air reacts with radiation-induced radicals and forms -C=O and -C-O bonding, which increases the intensity of the above groups.

Generally, XPS studies reveal that significant chemical changes occur after irradiation treatment. The significant increase in the oxygen content is attributed to the irradiation treatment, which may break the long molecular chains on the surface of the specimens and form the low-molecular weight oxygen-containing groups. The number of chain scissions increases with the increase in exposure time. These low-molecular weight oxidized species can be related to the AFM results as indicated by the straight pillars in the AFM images.

4 Conclusions

TPU film is one of the most versatile materials today. The wide application of TPU films requires the understanding of the surface properties and aging characteristics that improve stability and weatherability, which are important prerequisites to obtain appropriate products for high performance applications such as in aggressive environments. The current study specifically

aims to determine the effects of accelerated xenon lamp aging on the physical, chemical, and mechanical properties of TPU films.

The results of the mechanical tests for the TPU film indicate that this material is affected by photoaging, as observed in the significant changes in the mechanical properties. Changes in the morphology of TPU films after xenon lamp irradiation are observed by SEM. The micro-cracks and voids on irradiation-exposed surfaces can be observed. SEM photographs of the fracture surface of TPU films reveal that irradiation likely changes the ductile TPU films to their brittle form, which is in agreement with the mechanical test results. Surface topography is evaluated by AFM analysis. As the duration of exposure is prolonged, an increasing number of straight pillars at different heights, which correspond to the low-molecular weight oxidized species, also appear on the surface. R_a on the aged surface of the TPU films gradually increases. Results obtained from the FT-IR analysis of the accelerated aged samples indicate the deterioration of structural properties upon exposure to the accelerated aging environment. Longer irradiation time allows the formation of more oxygen-containing groups. XPS analysis shows that significant chemical changes in TPU films occur after irradiation treatment. Irradiation tends to break the long molecular chains and form the low-molecular weight oxygen-containing groups, which can be related to the AFM results that are represented as straight pillars in the AFM images.

In future studies, improving the weatherability of TPU films of airship envelope is important to resist the harsh stratospheric environment. The effect of coating on the TPU films will also be considered in our next study.

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