Degradation Study of Aromatic and Aliphatic TPU Films in Accelerated Weathering: Impact on the Gas Barrier and Mechanical Properties

Neeraj Mandlekar, Rishabh Tiwari, Sampath Parasuram, and Mangala Joshi

1 Introduction

Thermoplastic polyurethane (TPU) films and coatings are widely used for outdoor structures, inflatable systems and lighter than air (LTA) vehicles/systems due to a variety of excellent properties. TPU is also used as aerostat and airship design material [1]. However, like other polymeric materials, TPU is also susceptible to degradation when exposed to aggressive environments which significantly deteriorate the properties of TPU. Prolonged exposure under natural or artificial weathering causes irreversible degradation in chemical structure, mechanical properties and physical properties of PU films due to the presence of harmful UV radiation in the solar spectrum. As a consequence, the helium gas barrier and tensile properties of PU films are significantly affected and the overall service life of the LTA envelope is reduced. However, the weather resistance properties of PU films strongly depend on chemical structure and molecular chain orientation. It has been reported that aliphatic grade PU provides better weather resistance than aromatic grade PU [2].

In the last few years, the influence of the weathering process on the prediction of life of the envelope material has attracted increasing attention [3]. In this context, several studies have been proposed doing natural and artificial weathering tests [4–6]. However, natural weathering is most of the time is not repeatable due to dependency on several natural factors. Therefore, the artificial weathering test is more reliable to simulate natural weathering in controlled weatherometer apparatus [7, 8]. It has been reported that xenon arc-based light sources are widely used to simulate UV radiation from the Sun, and such artificial weathering has been demonstrated in several studies on the ageing characteristic of polymers and polymeric blends/composite s [9]. There are a few studies which have been carried out with polyurethane films and

N. Mandlekar (✉) · R. Tiwari · S. Parasuram · M. Joshi
Department of Textile and Fibre Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India
e-mail: neeraj.mandlekar@textile.iitd.ac.in

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coatings in xenon arc-based accelerated artificial weathering conditions using laboratory weatherometer [10, 11]. However, weathering environment has not been fully described using xenon lamp because it produces a higher relative intensity of shorter wavelength which simulate the extremely harsh environment more accurately. Thus, to simulate outdoor natural weathering in artificial weatherometer apparatus more environmental factors have to be incorporated.

Hence, in this work, accelerated artificial weathering process is particularly designed for testing of coated and laminated flexible textile material which is used in developing envelope of LTA systems. Such weathering condition especially gives the UV radiation in the range of 340 nm using glass filters, other weathering parameters like irradiance, humidity, temperature and wind speed are set to simulate natural weathering with a higher UV exposure rate. To study weather resistance properties aliphatic and aromatic polyether-based different types of TPU have been used to study the influence of accelerated artificial weathering on tensile properties, helium gas barrier and change in surface morphology.

2 Material and Method

2.1 Materials

Aromatic and aliphatic polyether-based thermoplastic polyurethane (TPU) polymer resins were procured from Lubrizole Advanced Materials, Europe, under the trade name of ESTANE®. Pellets were dried under vacuum for 3 h at 70 °C before transforming them into a continuous film.

2.2 TPU Extrusion Cast Film Preparation

Polyether-based aliphatic and aromatic TPU films used in this study were produced in the lab using a single screw extruder connected with cast film unit (LabTech Engineering, Model LCR 300 HD, Thailand). Single screw L/D 30 was used at predefined temperature profile 160, 170, 170, 180, 180 °C. Roller speed was maintained between 0.8 and 1 m/min to obtain a uniform thickness of continuous 100 μm film with 30 cm width. Figure 1 shows the single screw extruder and extrusion film casting assembly used for developing TPU films.

Fig. 1 Different stages of aliphatic and aromatic TPU film preparation by using single screw extruder connected with film casting unit

2.3 Artificial Accelerated Weathering Test

Artificial weathering tests were performed to evaluate the stability of the TPU films studied. ATLAS Xenotest 440 weatherometer was used, which simulates the severe outdoor environmental condition (see Fig. 2) The 2000 W xenon arc lamp was used to produce solar radiation, and a glass filter was used to exclusively allow 340 nm UV radiation. Weathering tests were carried out according to ISO 4892-2 standard, which is used to study artificial weathering tests for coated flexible textile materials. Both the aromatic and aliphatic films were exposed in the combined effect of irradiance, temperature, humidity and wind at different time intervals of a dry and a wet cycle. Irradiance was 0.51 $\pm$ 0.01 W/m^2, temperature 38 °C $\pm$ 1, fan speed 2000 rpm and relative humidity was 50% during dry cycle and 100% in wet cycle. A dry cycle was set for 102 min and a wet cycle for 18 min. These dry and wet cycles were repeated up to 500 h. Testing samples were taken out every 100 h to investigate the mechanical properties, helium gas barrier, surface morphology and chemical structure change.

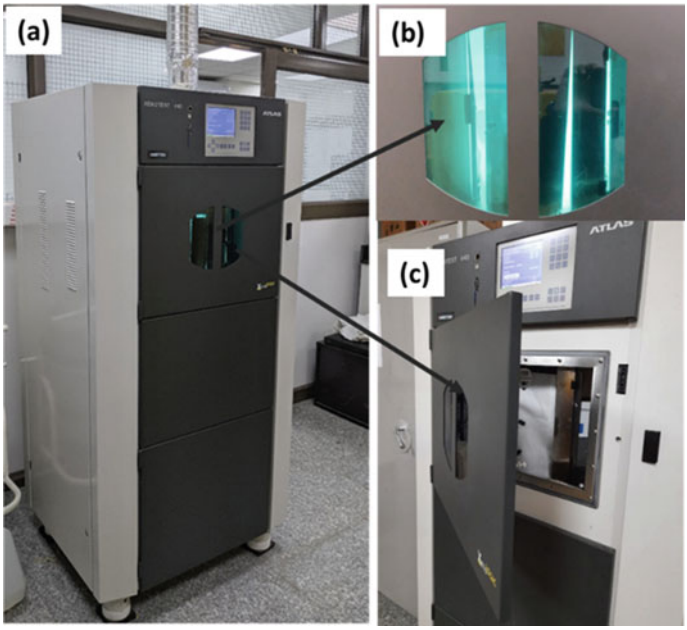

Fig. 2 Accelerated artificial weathering test: **a** laboratory weatherometer, **b** exposure chamber and **c** chamber with sample panel in spherical fashion

2.4 Characterization Techniques

Following characterization techniques were used to evaluate the weather resistance properties of the exposed TPU films.

Tensile Testing. Mechanical strength of exposed films was measured in INSTRON tensile testing machine (Model no 5960), USA. Load cell with 5 kN capacity was used, and tests were carried out in tensile mode with specimen size 10 cm × 2.5 cm keeping extension rate 500 mm/min according to ASTM standard D882. Results were extracted from Bluebill software, and breaking strength, modulus and % elongation were reported.

Helium gas permeability. Low helium gas permeability is a critical requirement of any LTA system. For artificial weathered films, helium gas permeability was measured according to ASTM D1434 using Labthink, Classic 216 gas permeability tester. Tests were carried out through the differential pressure method in proportional mode with helium gas pressure 100 kPa and test area was 38.48 cm^2. The helium permeability test was repeated three times for each sample.

ATR-FTIR analysis. Change in chemical structure was assessed by FTIR analysis in ATR mode using Nicolet iS50 Thermoscientific with ZnSe crystal. Spectra were

recorded at room temperature in the range from 4000 to 500 cm^{-1} using 64 scans with 4 cm^{-1} optical resolution.

SEM analysis. Surface morphology of unexposed and exposed TPU films was studied in ZEISS Ev18 apparatus equipped with an X-ray probe (INCAEnergy Oxford, Cu Ka X-ray source, k ¼ 1.540 562 Å), under the voltage of 20 kV. The sample was cut in 2 mm^2 shapes and placed on carbon tape and sputter-coated with the gold layer.

AFM analysis. The surface roughness of exposed TPU films was assessed by AFM analysis. When the exposed films were removed from a weatherometer chamber after different exposure time intervals, a 5 mm^2 square specimen was cut for AFM studies. The AFM used in this work was a Nanoscope IIIa (Digital Instruments, California). A "J" scanner (125 μm scan region) was employed to collect the topography of 20 μm^2 region. The collected 2D AFM images were processed by Gwyddion software to obtain 3D AFM images.

UV protection factor measurement. The ultraviolet protection factor (UPF) of TPU films was measured for unexposed and exposed TPU film samples. Testing was performed according to standard AATCC 183:2000, by a UV transmittance analyser (Labsphere 2000F) over a wavelength range of 290–450 nm. For each sample, scanning was done at ten different places, and an average was taken to calculate the % UV transmittance and UPF rating.

3 Results and Discussion

3.1 Mechanical Properties

Tensile properties of TPU films evaluated before and after the exposure shows that the aromatic and aliphatic TPU films behave differently during tensile testing (see Fig. 3). Tensile testing results are collected in Table 1. In aliphatic TPU films as the exposure time increases breaking strength and % elongation abruptly increase in 100 h due to the formation of stronger bonds which allows to better stress transfer resulting in higher breaking strength. Further, increasing the exposure time gradually reduces the breaking strength and % elongation, at the same time modulus increases up to 500 h but after that, film material degraded and start behaving like soft material and all tensile parameters decreased. This is ascribed to the scission of longer polymer chains into shorter chains due to the degradation under artificial weathering (UV exposure). Besides, aromatic TPU films also show similar behaviour in 100 h and increment in breaking strength, % elongation noticed thereafter increasing the exposure time lower the breaking strength and % elongation, at the same time, modulus increases with longer exposure time. This behaviour is attributed to the crosslinking in the polymer chains caused by UV radiation. After 300 h of exposure, aromatic TPU film becomes brittle material because the modulus value significantly increases but other

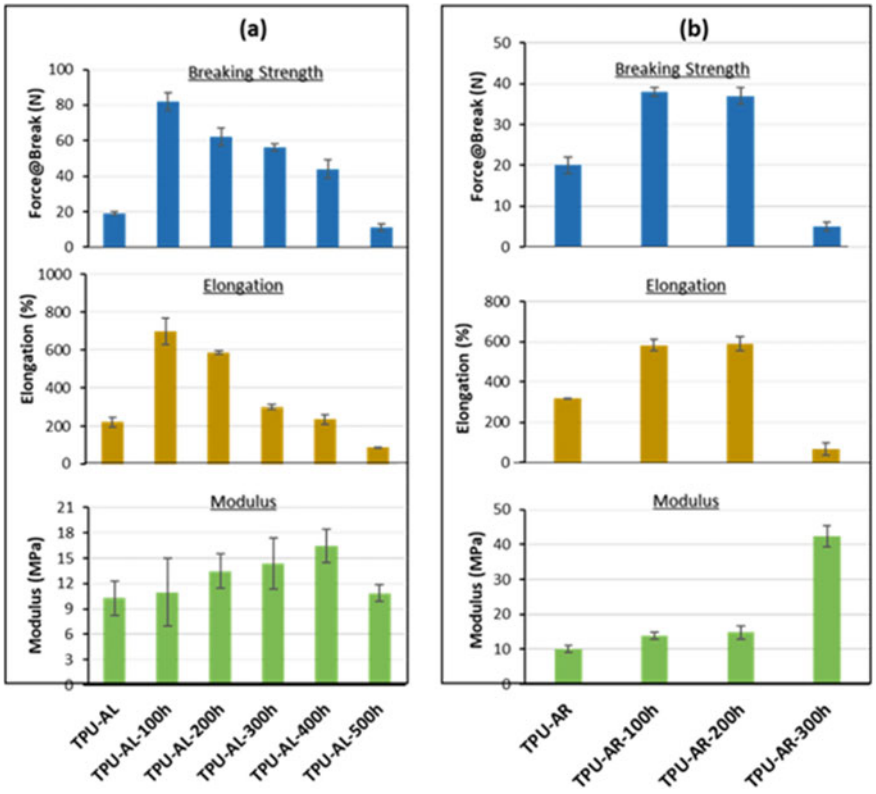

Fig. 3 Tensile properties of aliphatic and aromatic TPU films after exposure; (a) TPU-AL and (b) TPU-AR films

tensile parameters decreased which is attributed to the crosslinking behaviour in aromatic TPU film. This crosslinking behaviour is also confirmed by FTIR analysis.

3.2 Helium Gas Permeability

Helium gas barrier is one of the most important properties of LTA envelope material, and TPU films are used in designing weather resistance and gas barrier layers material. Helium gas permeability study of aliphatic and aromatic TPU exposed film exhibit opposite behaviour to each other. Helium permeability of artificial weathered TPU films is shown in Fig. 4a–b and data is collected in Table 2. In order to get extrapolated values for a longer duration of exposure, the polynomial curve fitting equation was used, and data was extrapolated up to 900 h exposure time. Helium barrier results of TPU-AL film show that permeability was slightly changed up to 500 h exposure. This behaviour shows that aliphatic film has weather resistance

Table 1 Tensile properties of exposed aliphatic and aromatic TPU films

Sample code	Breaking strength (N/2.5 cm)	Modulus (MPa)	Elongation (%)
TPU-AL	19 ± 1	10.26 ± 1	222 ± 25
TPU-AL-100 h	82 ± 5	10.97 ± 3	700 ± 70
TPU-AL-200 h	62 ± 4	13.47 ± 2	586 ± 10
TPU-AL-300 h	56 ± 2	14.38 ± 3	300 ± 12
TPU-AL-400 h	44 ± 4	16.47 ± 2	235 ± 24
TPU-AL-500 h	11 ± 2	10.85 ± 1	80 ± 4
TPU-AR	20 ± 2	10.1 ± 2	316 ± 30
TPU-AR-100 h	38 ± 1	13.82 ± 5	582 ± 28
TPU-AR-200 h	37 ± 2	14.76 ± 2	589 ± 36
TPU-AR-300 h	5 ± 1	42.38 ± 3	67 ± 31

properties as far as helium permeability is concerned. However, extrapolated data shows that even after 900 h exposure TPU-AL film has helium permeability up to 4.5 L/m^2/24 h.

Conversely, when TPU-AR film was exposed in artificial weathering initially helium barrier increased as exposure time increases up to 300 h which is attributed to the molecular rearrangement that leads to the crosslinked structure in aromatic TPU film, and increasing exposure time gives a higher helium permeability value because the cracks were observed on the surface of aromatic TPU films, these cracks on film surface were also confirmed by SEM analysis. When this data is extrapolated using the polynomial equation, the value of helium permeability is significantly decreased in 900 h which shows permeability up to 30 L/m^2/24 h. Practically, film loses its helium retention property after 900 h. This finding concludes that aromatic film is seriously degraded under UV exposure.

3.3 Surface Degradation

Surface morphology: Surface degradation of TPU films was also assessed by surface morphology and surface topography analysis. SEM analysis was used to study surface roughness and cracks on exposed TPU films (see Fig. 5). SEM micrograph of aliphatic TPU film shows that the surface of the film remain smooth as there were no cracks observed, except slightly roughness on the surface after 500 h. However, SEM micrograph of aromatic TPU film shows cracks after 500 h exposure in artificial weathering, there were clear cracks noticed; however, film still has helium permeability around 1.9 L/m^2/24 h, and it means that these cracks are formed only on the top surface. This finding concludes that aliphatic film is more stable in UV exposure than aromatic film.

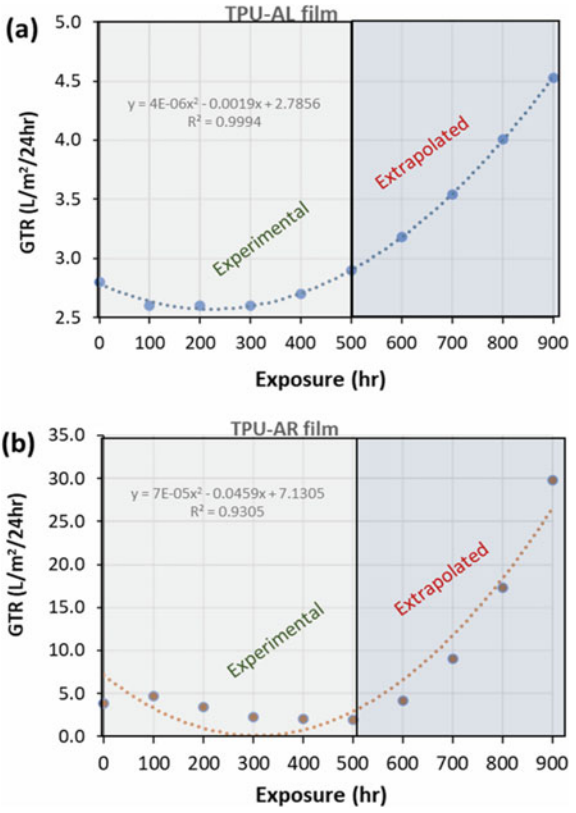

Fig. 4 Helium gas permeability of aliphatic and aromatic TPU film experimental and extrapolated data curve; **a** TPU-AL and **b** TPU-AR films

Table 2 Helium gas permeability of unexposed and exposed TPU films

Samples	Helium gas permeability (L/m^2/24 h)					
	Exposure time					
	0 h	100 h	200 h	300 h	400 h	500 h
TPU-AL	2.8	2.6	2.6	2.6	2.7	2.9
TPU-AR	3.8	4.7	3.4	2.3	2	1.9

Surface topography: Surface roughness was also evaluated by AFM analysis through tapping probe taking a testing area of 20 μm^2. Figure 6 shows the 3D images of AFM analysis after 500 h exposed films of TPU-AR and TPU-AL. Similar to SEM micrographs, AFM images of TPU-AR also show a very high peak height of 61 nm and RMS roughness value of about 68 nm. This is attributed to the noticeable degradation of TPU-AR film during UV exposure in artificial weathering test. On the other hand, TPU-AL film exhibits only roughness at peak height up to 23 nm and RMS roughness around 14 nm. This finding indicates that TPU-Al film remains stable during UV exposure in artificial weathering.

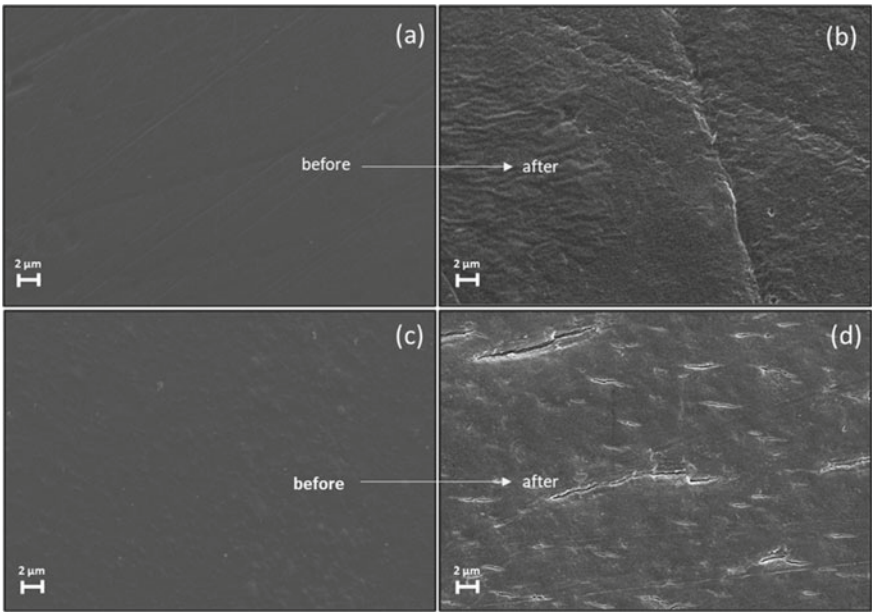

Fig. 5 SEM micrographs of TPU films surface before and after 500 h artificial weathering; **a** and **b** for TPU-AL, **c** and **d** for TPU-AR films surface

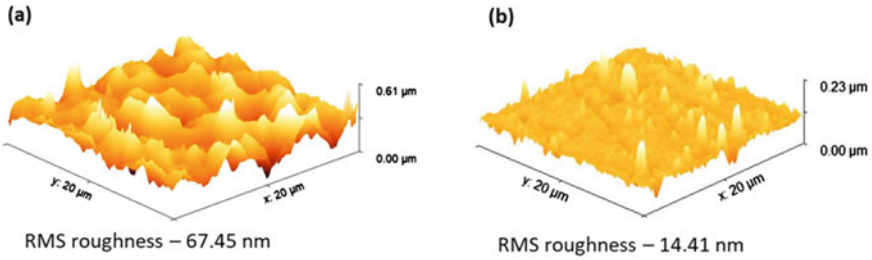

Fig. 6 AFM images of 500 h exposed aliphatic and aromatic TPU films; **a** TPU-AR-500 h and **b** TPU-AL-500 h

3.4 Chemical Structure

ATR-FTIR analysis was used to study the change in chemical structures after artificial weathering. Several characteristic peaks were assigned based on the literature study. Figures 7 and 8 represent the ATR-FTIR spectra of unexposed TPU film, 300 h and 500 h exposed film.

Aliphatic TPU film shows a characteristic peak at 3315 cm^{-1} due to the presence of N–H stretching of urethane linkage. The peak at 1680 cm^{-1} occurs due to the carbonyl stretching of urethane linkage in TPU. Other peaks at 1522, and 1450 cm^{-1}

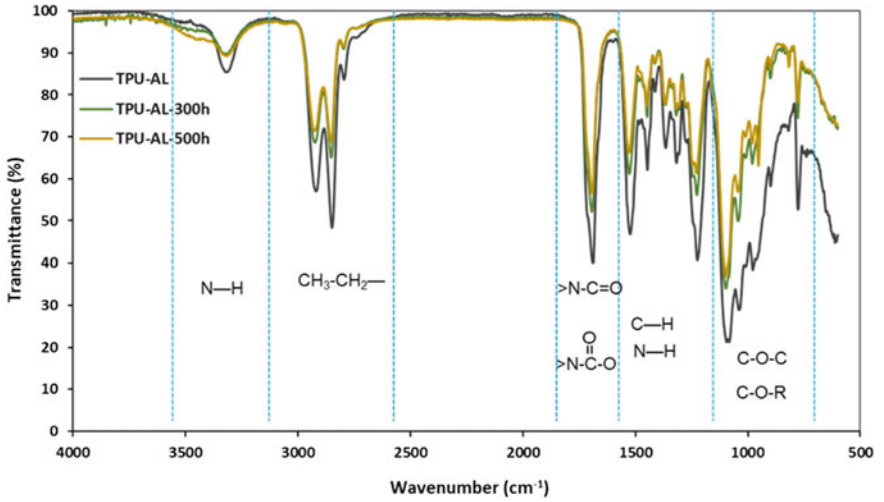

Fig. 7 FTIR analysis of aliphatic TPU films before and after exposure of 300 h and 500 h

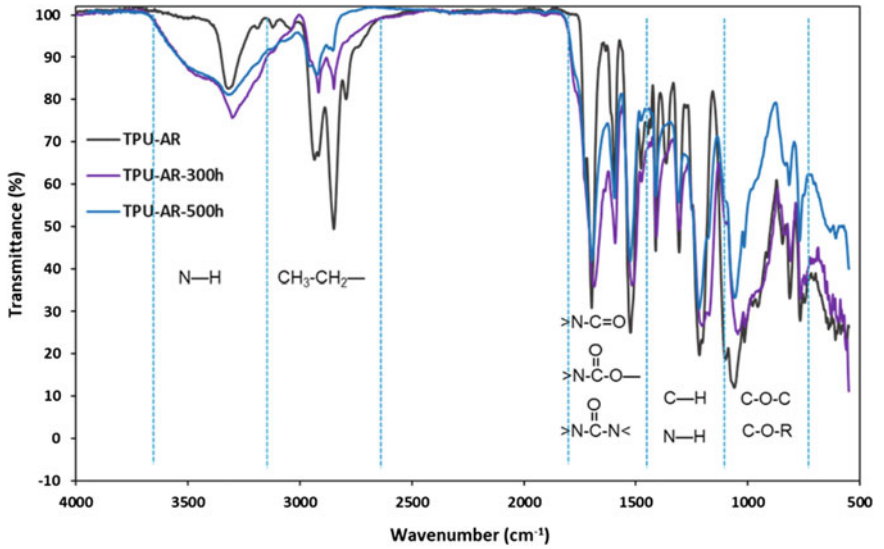

Fig. 8 FTIR analysis of aromatic TPU films before and after exposure of 300 h and 500 h

relates to C-H stretching as well as N–H vibrational peak and peak at 1215 cm^{-1} and 1052 cm^{-1} indicates the presence of C–O–C (ether) groups in TPU films. However, after weathering, TPU-AL film shows a reduction of these peaks due to UV exposure that breaks long molecular chains on the surface of the specimen and forms low molecular weight oxygen containing groups resulting in higher intensity of C-O-

peaks between 1250 and 1000 cm^{-1}. Similar characteristic peaks are identified in spectra of aromatic TPU film, peaks at 3315 cm^{-1} N–H stretching and peak at 1680 cm^{-1} C = O stretching due to the urethane linkage of TPU. Other peaks at 1522 and 1412 cm^{-1} relates to C-H stretching and peak at 1215 cm^{-1} and 1052 cm^{-1} indicates the presence of C–O–C groups. As the exposure time interval increases the peak at 1680 cm^{-1} and 3315 cm^{-1} decrease owing to the degradation in TPU-AR film and peak at 1590 cm^{-1} increases due to the formation of urea groups as result of degradation.

3.5 UPF Measurement

The ultraviolet protection factor (UPF) of any material is a measure of the effectiveness of protection against UV radiations coming through the solar spectrum. A higher UPF value of a material indicates low transmission of UV radiation resulting in better protection from degradation by UV. Figure 9 shows the UPF rating of unexposed and exposed aliphatic and aromatic TPU films at different exposure times. The UPF value of both types of TPU films was 52 with unexposed samples. UPF is gradually increased with exposure time interval and reached 140 after 400 h due to structural changes in TPU thereafter reduced to a value of 55 after 500 h exposure due to degradation of molecular chains. Similar behaviour was observed in tensile properties. Conversely, aromatic TPU film shows practically no change up to 200 h exposure, and then it increases up to 310 after 500 h. this increase in UPF could be attributed to the crosslinked TPU structure and yellowing in TPU leading to the partial absorption of UV radiation and resulting in the lowering in the UV transmission.

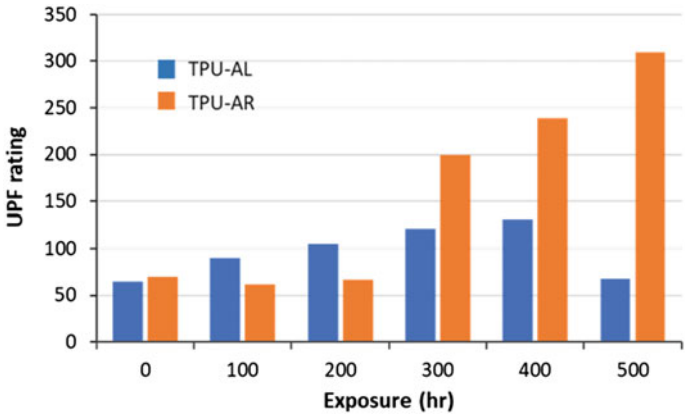

Fig. 9 Change in UV protection value of aromatic and aliphatic TPU films before and after artificial weathering tests

4 Conclusion

TPU-based coating and films are used in designing the envelop structure of LTA systems. The weather stability of these materials is crucial in order to determine the service life of the overall LTA structure. The chemical structure of TPU plays a critical role to determine the weather resistance behaviour. In this work, accelerated artificial weathering is performed to carry out the exposure study. Artificial weathering parameters were specially designed to simulate outdoor natural weathering with a higher exposure rate to UV radiation. Exposure tests carried out on aliphatic and aromatic TPU showed different weather resistance behaviour. With increasing, exposure time TPU film shows improvement in tensile properties at the beginning but further increasing exposure interval leads to the reduction in tensile properties. After 500 h of exposure, both the aliphatic and aromatic TPU film lost the breaking strength of more than 50% than that of unexposed films. Similarly, helium gas permeability initially decreased up to 500 h, and then, films start losing the helium barrier. The aromatic film shows the cracks formation on the surface that led to the loss of the helium barrier. ATR-FTIR analysis also confirms the crosslinked structure formation. This study concludes that aliphatic TPU has more weather resistance properties than aromatic TPU film, which has more reactive groups susceptible to UV degradation during artificial weathering.

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