

Influence of Environment on Ageing Behaviour of the Polyurethane Film

Yanzhi WANG^{1*}, Zonghui SUN¹, Jifeng TIAN², Haiyan WANG¹, Huicong WANG¹, Yingliang JI¹

¹ Hebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P.R. China

² College of Civil Engineering & Mechanics, Yanshan University, Qinhuangdao 066004, P.R. China

crossref <http://dx.doi.org/10.5755/j01.ms.22.2.12935>

Received 20 August 2015; accepted 19 December 2015

In this work, UV-Vis spectra, FT-IR spectra, colour difference, yellowness index, and SEM micrographs were used to study the accelerated ageing behaviour of polyurethane films that exposed to UV radiation, O₃ atmosphere, and UV/O₃ integrated environment. During 200 hours of exposure in three different environment, the UV absorbance, the colour difference, the yellowness, and the absorption of –NH–OH and –C=O bands in FT-IR spectra of the films increase gradually with increasing exposure time, respectively, and the films exposed to the three environments have different colour difference, yellowness index, UV-Vis spectra, and FT-IR spectra. The films are vulnerable to degradation and yellowing in the following environment order: O₃ < UV < UV/O₃. After exposure to UV radiation or O₃ atmosphere, some degradation products and blisters are formed on the film surface. After exposure to UV/O₃ integrated environment, there are strip blisters and micro-cracks on the film surface, and exists an obvious synergism between UV radiation and O₃ atmosphere in accelerating the ageing of the polyurethane films.

Keywords: polyurethane films, ageing, synergism.

1. INTRODUCTION

Thermoplastic polyurethane are AB-type copolymers of alternating soft and hard segments [1]. Recently, the thermoplastic polyurethane is becoming one of the outstanding candidate materials for aircraft weathering layer or high-altitude balloon, because it has excellent performances, such as chemical resistance, high-flexibility and good adhesion with other materials. However, one of the particular disadvantages of the polyurethane materials is their extreme sensitivity to some environments such as UV radiation, temperature, humidity and so on. This is a major limitation which relates to their use as surface coatings in outdoor applications. Many papers [2–8] have been published on the degradation of polyurethane material, including oxidation initiated by heat and light, hydrolysis, thermolysis, and degradation at high temperatures, etc. In addition, atmospheric ozone usually causes the degradation of polymers. Ozone concentrations of less than 1 ppb can severely attack non-resistant elastomers if they are in the strained condition. Therefore, ozone attack is often the most important effect on properties of polymer exposed to space environment. Nowadays the ozone resistance of polymer products is of paramount importance, because the problem has worsened as atmospheric ozone concentrations have gradually increased [9].

If the polyurethane materials are applied to the aircraft weathering layer or the high-altitude balloon, the polyurethane film will be exposed to harsh environments including UV radiation and O₃ atmosphere. The internal molecular structure of the polyurethane film may change continuously, resulting in the changes of the chemical and physical properties of the materials. However, commercial

the polyurethane material are chemically complex, and contain thermally and hydrolytically labile groups such as urea, isocyanurate, ester, and ether moieties, as well as various additives. Therefore, it is not simple to assess their present state of stability and remaining service life. Accelerated ageing tests can be used to assess ageing behaviour of the polyurethane films over a short time. The research could provide effective data support for the application of the polyurethane material in aircraft weathering layer or high-altitude balloon, and help to design new ones. This is a challenge to those who care for such items.

Our research group studied effects of additives on weather-resistance properties of polyurethane films exposed to ultraviolet radiation and ozone atmosphere [10]. Until now, we have not found other literature compared the accelerated ageing behaviour of the polyurethane film exposed to UV radiation, O₃ atmosphere and UV/O₃ environment. In this study, the accelerated ageing behaviour of polyurethane films exposed to UV radiation, O₃ atmosphere, and UV/O₃ integrated environment was investigated, respectively, and whether there was synergism between UV radiation and O₃ atmosphere in accelerating the ageing of polyurethane films was also analysed.

2. EXPERIMENTAL DETAILS

2.1. Materials

Polyether polyurethane (PU) pellet was purchased from BASF SE Co. (Germany), N,N-dimethylformamide (DMF) (AR.) was purchased from Tianjin Kay Tong Chemical Reagent Co., Ltd.(Tianjin, China). Butanone (AR.) was purchased from Tianjin Sailboats Chemical Reagent Technology Co., Ltd. (Tianjin, China).

* Corresponding author. Tel.: 0335-8061569; fax: 0335-8061569.
E-mail address: hwyz@ysu.edu.cn (Y. Wang)

2.2. Specimen preparation

The mixed solvent was obtained by mixing DMF and butanone in the mass ratio of 7:2. Polyurethane pellets of 50 g were gradually added to the mixed solvent of 50 g according to the mixed solvent and the pellets with the mass ratio of 1 to 1, and the above mixture was slowly heated to about 60 °C, and the mixture was vigorously stirred for 2 h, and then the slurry with 12–13 wt.% solids content was obtained. In this experiment, the films for exposure experiments were prepared by using a spin coater at the rate of 2000 r/min for 5 s, dried in a vacuum oven at 50 °C for 12 h. Calcium fluoride discs with a thickness of 2 mm and a diameter of 25 mm were selected as the substrate of PU films because CaF₂ discs have excellent moisture, heat resistance properties, and it is transparent to both UV-visible and infrared radiation. Because the films substrate for testing SEM micrographs should be conductive, and CaF₂ disc is not conductive, the films for testing SEM micrographs were coated on the hard aluminum foil by using a coating machine at the rate of 6 cm/s. The films thickness is approximately 100 microns. The films were dried in a vacuum oven at 50 °C for 12 h. The obtained PU films with thickness of 12–13 μm were placed in a desiccator.

2.3. Ageing tests

The ageing tests of PU films were carried out in a self-designed ageing device. UVB-313 fluorescent UV lamp (U.S. Q-Lab Corporation, 290 nm < λ < 400 nm) was used as a light source, and AD-XF-5 P ozone machine (Jinan Jie Anritsu Technology Co., Ltd.) was used as an ozone source in the ageing device. UV irradiation intensity was 400 ± 20 μW/cm², and the ozone concentration was 100 ± 2 ppm. UV ageing, O₃ ageing and UV/O₃ integrated ageing were performed with the films at ambient relative humidity, respectively. The ageing time of the films was 20 h, 60 h, 120 h, 160 h, and 200 h.

2.4. Properties characterization

UV-Vis spectra of all the films were collected on UV-2550 UV-Vis spectrophotometer (Shimadzu Corporation, Japan) in the wavelength range of 190–800 nm at 0.5 nm increments. All FT-IR spectra in transmission mode were collected on a Nicolet iS10 infrared spectrometer (Thermo Fisher Scientific) in the wave number range of 400–4000 cm⁻¹. Spectral resolution of 4 cm⁻¹ was used. The colour difference and the yellowness index of all the films after exposure were recorded using a CR-10 colorimeter (Konica Minolta Corporation, Japan). The Scanning Electron Microscopy (SEM) studies were performed using S-4800 field-emission scanning electron microscope (Hitachi Limited), and the operating voltage was 15 kV. The sample surface was sprayed with gold prior to imaging.

3. RESULTS AND DISCUSSION

3.1. UV-Vis spectra

UV-Vis spectra of PU films exposed to UV radiation, O₃ atmosphere and UV/O₃ integrated environment at the different exposure time are shown in Fig. 1.

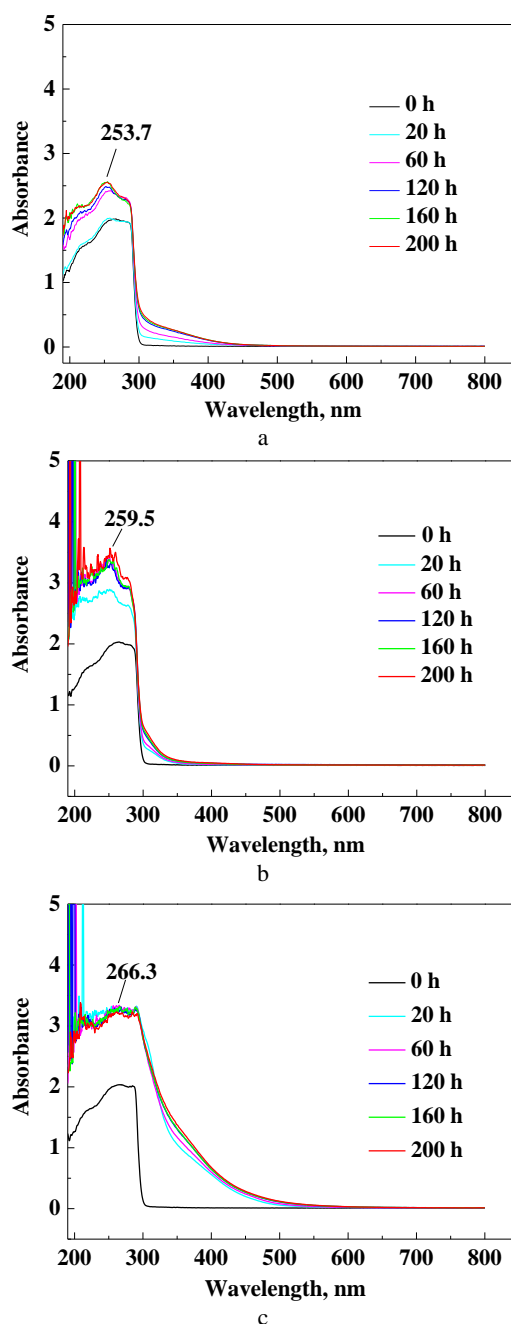


Fig. 1. a – UV-Vis spectra of PU films exposed to UV radiation; b – UV-Vis spectra of PU film exposed to O₃ atmosphere; c – UV-Vis spectra of PU film exposed to UV/O₃ integrated environment

As can be seen, UV-Vis absorbance gradually increases with prolonged exposure time, indicating that the ageing degree of PU films gradually deepens. Secondly, the absorption peaks near 200 nm, which are ascribed to the n- π^* transition from carbonyl groups, gradually increase and widen with prolonged exposure time. It suggests that the amount of carbonyl compounds is continuously increasing, and the type of carbonyl compounds is constantly transforming during the exposure in O₃ atmosphere and UV/O₃ integrated environment [8]. Thirdly, a bathochromic shift is observed in the range of wavelength greater than 300 nm in Fig. 1. This indicates that PU molecule may be partially transformed into a quinine-imide chromophore during the degradation process [8]. The films exposed to various environments have

different bathochromic shift in UV-Vis spectra. The environment order of the bathochromic shift is as follows, $O_3 < UV < UV/O_3$. This suggests that the films are vulnerable to degradation and yellowing in the above environment order.

3.2. FT-IR spectra

Fig. 2 shows FT-IR spectra of PU films exposed to UV radiation, O_3 atmosphere and UV/O_3 integrated environment at different exposure time. As it can be seen, the absorption peaks between $3700-3000\text{ cm}^{-1}$ characterizes N-H and O-H stretch vibrations. The peak at ca. 1720 cm^{-1} can be assigned to C=O stretching vibration in ester structure, 1531 cm^{-1} N-H deformation (amide II band), 1416 cm^{-1} C-N stretching. The region of $1300-1100\text{ cm}^{-1}$ is characteristic of C-O stretching vibration in urethane structure. The absorption peak at ca. 1597 cm^{-1} could be attributed to C=C skeletal vibration in aromatic ring. While the vibrational modes between 3000 cm^{-1} and 2800 cm^{-1} can provide strong indication of C-H stretching. The changes in FT-IR spectra exhibit a number of interesting and novel groups associated with polyurethane [8]. The changes of the main functional groups are summarized in Table 1.

Table 1. FT-IR absorption band changes of the films exposed to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment

Wavenumber, cm^{-1}		Absorption band
Increase	Decrease	
3500–3200		–NH/–OH stretching vibration
	2940	asymmetrical stretching vibrations of the CH_2 group
	2850	symmetrical stretching vibrations of the CH_2 group
1763–1640		–C=O stretching of the urethane
	1600	the stretching vibration of the double bonds in the aromatic ring
	1530	the coupling peak of –NH bending and –CN stretching motion
	1230	–C–C stretching peak
3500–3200	1110	–C–O absorption peak

As it can be seen, the absorption in the region of $3500-3200\text{ cm}^{-1}$ significantly increases. This suggests the formation of hydroxyl groups in PU films. The absorption in the region of $2390-2270\text{ cm}^{-1}$ is a noticeable phenomenon in Fig. 2 c, which may be attributed to the formation of –NCO during UV/O_3 ageing process [10]. The increase of the absorption in the region of $1763-1640\text{ cm}^{-1}$ indicates that new carbonyl species including quinine-imide structure may generate [11]. The peaks at 1530 cm^{-1} , 1230 cm^{-1} and 1110 cm^{-1} gradually decrease as a function of exposure time. These suggest that the bonds of –C–O and –CN break, and the bonds of –C=O, –NH and –OH appear in the molecules of PU films during exposure [12]. A loss of the peak intensity at 1600 cm^{-1} could be attributed to the conversion of benzene ring to quinine or azo structure, which may be the reason for yellowing of the films [14, 15]. At the same time, there is different degree of the variation for the above-mentioned peaks in different environments. The order of the variation degree in various

environment is as follows, $O_3 < UV < UV/O_3$. This suggests that the films are vulnerable to degradation and yellowing in the above order. These are basically consistent with the results of the UV-Vis spectra.

3.3. Colour change and synergistic ageing effect

The colour difference of PU films exposed to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment are shown in Table 2. “ $UV+O_3$ ” represents algebraic sum of the colour difference of the film exposed to UV radiation and that to O_3 atmosphere at the same time. It can be seen that the colour difference of PU films exposed to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment increase with increasing exposure time, respectively.

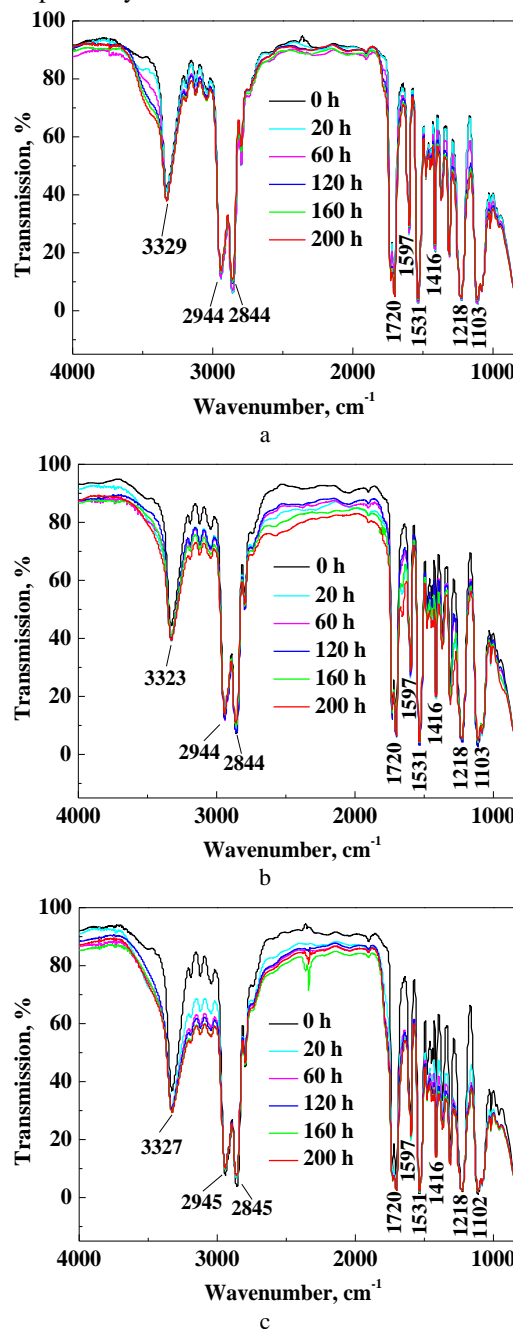


Fig. 2. a–FT-IR spectra of PU films exposed to UV radiation; b–FT-IR spectra of PU films exposed to O_3 atmosphere; c–FT-IR spectra of PU films exposed to UV/O_3 integrated environment

Secondly, the films exposed to various environments have different colour difference. The colour difference order is as follows, $O_3 < UV < UV/O_3$, which suggests that the films are vulnerable to degradation and yellowing in the above environment order. Thirdly, the colour difference of the film exposed to UV/O_3 integrated environment is significantly greater than the value of “ $UV + O_3$ ” at the same time. This suggests that an obvious synergistic ageing effect between UV ageing and O_3 ageing exists when the colour difference is used as the evaluation index. This may be explained by the phenomenon that atomic oxygen generated from ozone accelerates the loss of the activity of the polymer chain in the ultraviolet irradiation.

Table 2. The colour difference of PU film exposed to various environments

Environment	Time, h					
	0	20	60	120	160	200
UV	0	4.35	4.00	5.60	6.15	6.15
O_3	0	0.60	1.70	2.65	2.90	3.40
O_3/UV	0	34.00	38.30	40.05	39.65	40.85
O_3+UV	0	4.95	5.70	8.25	9.05	9.55

Table 3 demonstrates the yellowness index of PU films exposed to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment, in which “ $UV + O_3$ ” represents algebraic sum of the yellowness index of the film exposed to UV radiation and that to O_3 atmosphere at the same time. The changed rule of the yellowness index is consistent with that of the colour difference of the films exposed to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment. Secondly, the films exposed to various environments have different yellowness index. The order of the yellowness index is as follows, $O_3 < UV < UV/O_3$. This suggests that the films are vulnerable to degradation and yellowing in the above environment order. Thirdly, an obvious synergistic ageing effect between UV ageing and O_3 ageing exists when the yellowness index is used as the evaluation index.

Table 3. The yellowness index of PU film exposed to various environments

Environment	Time, h					
	0	20	60	120	160	200
UV	0	4.25	3.85	5.35	6.00	6.00
O_3	0	0.45	1.10	2.20	2.50	3.05
O_3/UV	0	33.50	37.80	39.30	38.75	39.80
O_3+UV	0	4.70	4.95	7.55	8.50	9.05

The colour difference of the films exposed to UV radiation is significantly greater than that to O_3 atmosphere at the same time, and the yellowness index of the film

exposed to UV radiation is significantly greater than that to O_3 atmosphere at the same time. This means that the degradation of the film induced by UV radiation is significantly greater than that induced by O_3 atmosphere. The probable reasons are as follows, ozone-induced oxidation reaction is a selectivity process with the low rate, and dipolar structure in ozone can react with the unsaturated bond, causing the breakage of the bond. Energy provided by UV radiation is enough to break the chemical bonds in polyurethane, and the internal structure of the polyurethane is not easy to be oxidized directly without the activation of ultraviolet [14]. Therefore, the polyurethane is more sensitive to UV radiation.

3.4. SEM micrograph

Fig. 3 presents SEM micrographs of PU films before and after 200 h exposure of UV radiation, O_3 atmosphere, and UV/O_3 integrated environment. Fig. 3 a shows that the surface of the unexposed PU film is relatively smooth and uniform. Fig. 3 b shows that some noticeable degradation products with different size are formed on the film surface after 200 h of O_3 exposure. The probable reasons are as follows, a part of the polymer chain in the film is broken and benzene ring is opened after the erosion of atomic oxygen generated from ozone. This leads to the macromolecular particles escaping. The uppermost layer of the film without any cracks is still relatively ductile and coherent, indicating that ozone only causes the degradation of the film surface layer [15]. Fig. 3 c shows that some blisters with different size and depth are formed on the film surface, and some blisters have broken after 200 h of UV exposure. It can be speculated that blisters are formed on the film surface during the initial phase of film degradation. These blisters increase in size continuously and finally break with increasing exposure time. These blisters may be attributed to the degradation of the film exposed to UV radiation, which resulted from the scission of the molecular chain in the film and the release of the gas [16–18]. Fig. 3 d shows that not only the surface, but also the bulk of the film is degraded. A large number of strip blisters cover the film surface, in which some blisters are formed, and some blisters have shrunk. The micro-cracks in all directions are formed throughout the film surface. The probable reasons are as follows, in the presence of ultraviolet radiation, the ozone is excited to generate more active oxygen atom, which causes the degradation of film surface and the increase of the degradation products of the films. Meanwhile, the ozone can easily act on the interior of the film due to the generation of cracks and accelerate the degradation of the polyurethane film [19].

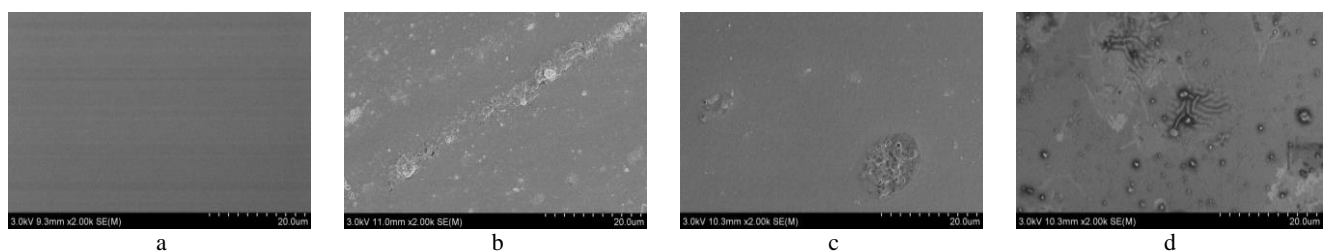


Fig. 3. a – SEM images of PU film surface before exposure; b – after 200 h exposure in O_3 atmosphere; c – after 200 h exposure in UV/O_3 integrated environment; d – after 200 h of UV radiation

This suggests that the films are vulnerable to degradation in following environment order: $O_3 < UV < UV/O_3$, and an obvious synergism between UV and O_3 exists in accelerating the degradation of the polyurethane film.

4. CONCLUSIONS

1. UV absorbance, the colour difference, and the yellowness index of the polyurethane films gradually increase with increasing exposure time during exposure to UV radiation, O_3 atmosphere, and UV/O_3 integrated environment, respectively. The absorption of the main functional groups of $-NH/OH$ and $-C=O$ bands in FT-IR spectra gradually increase with increasing exposure time. Some degradation products and blisters are formed on the film surface after exposure to O_3 atmosphere and UV radiation, respectively. There are strip blisters and micro-cracks on the film surface after UV/O_3 exposure.
2. The films exposed to various environments have different the colour difference, the yellowness index, UV-Vis spectra, and FT-IR spectra. The films are vulnerable to degradation and yellowing in following environment order: $O_3 < UV < UV/O_3$.
3. An obvious synergism between UV and O_3 in accelerating the ageing of the polyurethane films exists.

Acknowledgement

The authors acknowledge Aerospace Science and Technology Innovation Fund for providing financial support for this study (Grant No. 2014-YF-0416).

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