



Synergistic Aging Effect of Polyether Polyurethane Coatings

H.Y. WANG, Y.Z. WANG*, Y.F. JIANG and X.S. LI

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

*Corresponding author: Tel./Fax: +86 335 8061569; E-mail: hhwyz@ysu.edu.cn

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The pure polyether polyurethane (ETPU) and the modified polyether polyurethane (M-ETPU) coatings containing composite additives were prepared by spin-coating technique. The accelerated aging tests of the coatings exposed to constant UV radiation with an ozone atmosphere were carried out by using a self-designed aging equipment. The aging resistance properties of the coatings were evaluated by UV-visible spectra, Fourier transform infrared spectra, yellowness index, photo-oxidation index and carbonyl index analysis. The results show that the ozone and ultraviolet initiate autoxidation of urethane bridge in the polymer chain to quinone-imide structure and trigger formation of hydroperoxides and new carbonyl species. The aging of the coatings increases with incremental exposure time, the aging of M-ETPU coating is much lower than that of ETPU coating at the same condition. There is distinct synergistic aging effect when the yellowness index, the photo-oxidation index and the carbonyl index is used as evaluation index, respectively.

Key Words: Polyether polyurethane, O₃/UV-aging, Synergistic aging effect.

INTRODUCTION

Polyether polyurethane (ETPU) elastomer is an important polymer possessing a variety of useful properties, including high impact strength, high elasticity and good adhesion. At present, it is now being increasingly used for the surface protection of materials like metals, plastics, wood, glass fibers, the aircraft industry as well as stratospheric airship¹⁻³. However, due to its sensibility to oxidative atmosphere and ultraviolet photooxidation degradation that would lead to discoloration and even total destruction, its use in outdoor applications is limited. Therefore, it is important to impart light stability to the ETPU coatings by modifying them with additives⁴. Additives can play a key role in determining the long-term aging performance of coatings. Generally both ultraviolet light absorbers (UVAs) and hindered amine light stabilizers (HALS) are often added to coatings to improve their performance and to screen the underlying layers from harmful radiation^{5,6}. The combination of HALS with UVAs absorber has been widely applied to improve the photostability of a variety of polymers^{7,8}. Hindered amine light stabilizers inhibit photooxidation by scavenging oxidation propagating free radicals, thereby reducing the number of the potentially reactive species in the coating. Ultraviolet light absorbers work by absorbing ultraviolet light that could otherwise initiate photo-oxidation. Recently inorganic nano-particles such as zinc

oxide⁹ and cerium oxide¹⁰ were also used as efficient UV absorbers to improve the performance of polyurethane coating.

The high-altitude airship and balloon are continuously exposed to stratospheric environment throughout their service life. High environmental resistance is necessary for ETPU, which is used as an economical candidate for the hull material of airship and balloon. Therefore it is important to study the ultraviolet and ozone aging induced degradation processes of ETPU coatings. The purpose of this study was to investigate the aging behaviour of ETPU material with and without additives exposed to UV with O₃ environment. The ingredients of the additives used in our experiments are the inorganic UV absorbers mixture (mixture of ZnO and CeO₂), the organic UV absorbers (mixture of UV-327 and UV-531), hindered amine light stabilizer (HALS-622) and antioxidant-1010.

EXPERIMENTAL

The pure ETPU material (1180A) was commercial grade from BASF Company. Organic UV absorbers of UV-531 and UV-327, antioxidant-1010 and HALS-622 used in this work were supplied by Nanjing Hua Lim Chemical Co., Ltd., China. The nano zinc oxide and nano cerium oxide used in this work were supplied by Nanjing High Technology of Nano Co., Ltd., China. The nano zinc oxide was surface treated with an organo-silane coupling agent in the supplied form.

The cerium oxide nanoparticles were modified with an organosilane coupling agent of γ -methacryloxypropyltrimethoxysilane (KH-570). The typical procedure was given as follows, 5 g of the pre-dried cerium oxide nanoparticles and 100 mL of the solvent mixture (ethanol/water with volume ratio of 3:1) were poured into a 250 mL three-neck flask and dispersed by ultrasonic irradiating at room temperature for 0.5 h. Then the suspension was heated to 85 °C. This step was followed by the slow addition of KH-570 (CeO₂/KH-570 with weight ratio of 6:100). The mixture was refluxed at 85 °C for 4 h under magnetic stirring. Modified nanoparticles were then filtered under suction and physically adsorbed KH-570 compounds were Soxhlet extracted with ethanol for 24 h and finally were dried at 80 °C in a vacuum oven for 12 h.

General procedure: The pure ETPU coatings and the modified ETPU coatings containing 1 wt. % inorganic UV absorbers mixture (ZnO/CeO₂ with weight ratio of 3:2), 0.6 wt. % organic UV absorbers mixture (UV-531/UV 327 with weight ratio of 1:1), 0.1 wt. % HALS-622 and 0.1 wt. % antioxidant-1010 (represented as M-ETPU coatings hereafter) were prepared according to the designed formulation. Calcium fluoride discs with a diameter of 25 mm and a thickness of 2 mm were selected as the substrate for the exposure study because it has excellent moisture and heat resistance properties and is transparent to both UV and infrared radiation^{11,12}, allowing for periodic characterization of spectral UV-visible and infrared radiation.

ETPU and M-ETPU coatings were applied to CaF₂ discs by spin-coating technique. For the first step, ZnO and CeO₂ nanoparticles were heated at 80 °C in a vacuum oven for 12 h to remove adsorbed moisture; the additives at the required ratio were directly added to the solvent mixture (DMF/butanone with volume ratio of 7:2) and dispersed by ultrasonic irradiating for 0.5 h. This step was followed by the slow addition of the stoichiometric amount of ETPU to the mixture; the mixture was slowly heated to 60 °C and then stirred vigorously for 2 h at a constant rate of 2000 rpm. The ETPU dispersion had a solid content of 15 ± 2 %. Subsequently, the composite was degassed and flooded onto the substrates and spun at 2000 rpm for 10 s. The coatings were then cured at 60 °C for 12 h.

The accelerated aging tests of ETPU and M-ETPU coatings were carried out by using a self-designed aging equipment, in which the intensity of UV and concentration of ozone can be well controlled, respectively. The source of UV radiation was fluorescent ultraviolet tubes (UVB-313EL type). According to test procedure, the specimens were continuously exposed to an ozone atmosphere of 25 ± 2 ppm (represented as O₃ hereafter), to constant UV radiation of 400 ± 20 μ W/cm² (313 nm) (represented as UV hereafter) and to constant UV radiation of 400 ± 20 μ W/cm² (313 nm) with an ozone atmosphere of 25 ± 2 ppm (represented as O₃/UV hereafter) at ambient temperature and relative humidity of 20 % for different time span with maximum exposure time of 600 h. Each sample was taken out after 50, 100, 150, 200, 350, 500 and 600 h of exposure for monitoring the degradation of the composite coatings by UV-visible spectra and FT-IR spectra, yellowness index, the photo-oxidation index and the carbonyl index of the coatings.

Detection method: Changes of yellowness index (YI) of coatings due to exposure were measured by using CR-10

(Minolta Co., Japan) colour difference meter. UV-visible spectra of the coatings and its changes during exposure were recorded by using UV-2550 (Shimadzu Co., Japan) spectrophotometer in the range of 200–800 nm at 0.5 nm increments. FT-IR spectra were measured by using Nicolet iS10 (Thermo Fisher Scientific Co., USA) spectrometer, the spectra were recorded in the range of 4000–400 cm⁻¹. According to FT-IR absorption spectra, the photo-oxidation index (PI) and the carbonyl index (CI) were calculated by eqns. 1 and 2, respectively,

$$PI = \left(\frac{A_{-OH,-NH}}{A_{-CH_3}} \right)_{aged} - \left(\frac{A_{-OH,-NH}}{A_{-CH_3}} \right)_{initial} \quad (1)$$

$$CI = \frac{A_{-C=O}}{A_{-CH_3}} \quad (2)$$

wherein, A_{-OH,-NH} is the area of the absorption band associated with -OH, -NH group, A_{-CH} is the area of the absorption band attributed to the C-H stretching band. The reference band will not be considerably affected by photo-oxidation. A_{-C=O} is the area of the carbonyl absorption band.

RESULTS AND DISCUSSION

UV-visible spectra: UV-visible absorption spectra of ETPU and M-ETPU coatings as function of exposure time are presented in Fig. 1. It can be seen that the absorption in the region of 334–411 nm increases with incremental exposure time for all coatings, which suggests that incident radiation in the wavelength range activates a urethane in an autoxidation process and the absorption in the region of 270–310 nm increases with increasing exposure time for all coatings, which suggest that some aromatic urethane groups in the polymer chains have autoxidized to a quinone-imide structure¹³. After 600 h of exposure, all coatings absorb relatively substantially more at 390–430 nm than at 565–750 nm and should be more yellow.

As can be seen, UV absorption increase of M-ETPU coating is distinctly lower than that of ETPU coating in the region of 270–310 nm after 200 h of exposure, which means aging extent of M-ETPU coating is distinctly lower than that of ETPU coating. As shown in Fig. 1, before aging, the absorbance curve of ETPU coating only shows an absorption peak at 200–290 nm, whereas the presence of composite additives in the M-ETPU coating has resulted in *ca.* 31 % increase in the absorption of 200–290 nm compared to ETPU coating and there is the other absorption peak in the higher UV region (300–400 nm). As such, UV light below approximately 450 nm can be efficiently absorbed by incorporating composite additives into a ETPU matrix. Therefore, the UV-aging resistance performance of M-ETPU coating is far superior to that of ETPU coating. However, the growth in absorption in the region of 200–270 nm was puzzling and further studies are needed.

FT-IR spectra: Fig. 2 presents the FT-IR spectra of ETPU coating before exposure and of M-ETPU coating before and after 600 h of exposure to O₃, UV and O₃/UV environment. It shows that the absorption peaks at *ca.* 3328 cm⁻¹ correspond

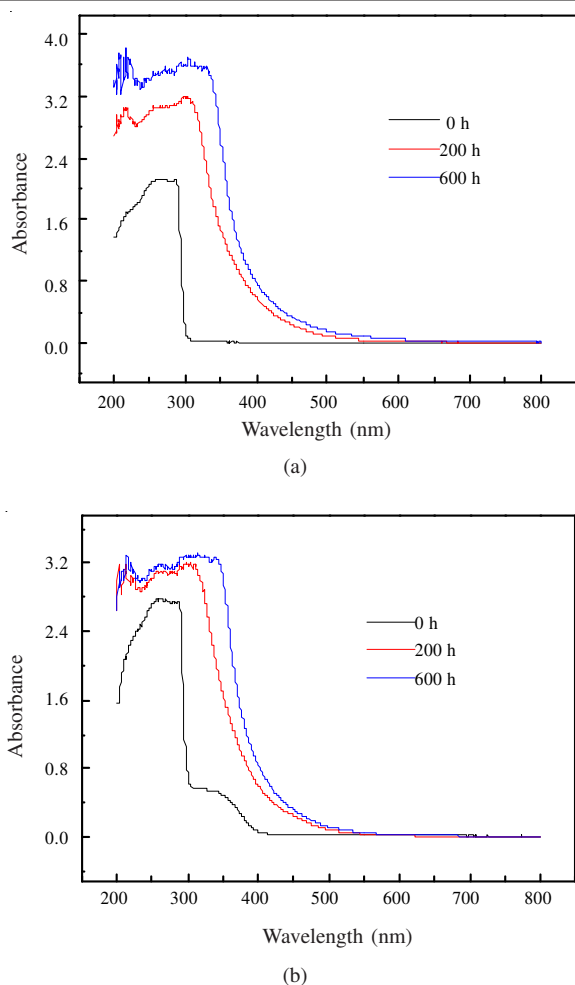


Fig. 1. UV-visible spectra of coatings as function of exposure time, (a) ETPU; (b) M-ETPU

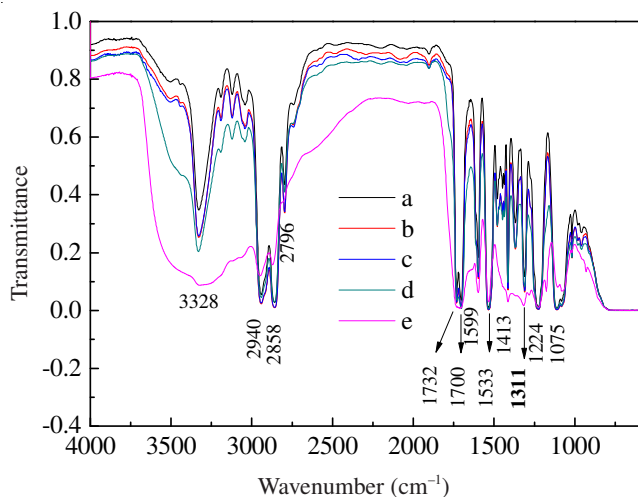


Fig. 2. FT-IR spectra of ETPU coating before exposure (a) and of M-ETPU coatings before exposure (b) and after 600h of exposure to O_3 (c), UV (d) and O_3/UV (e)

to N-H and O-H stretch, 1700 cm^{-1} C=O stretch (amide I band), 1533 cm^{-1} N-H deformation (amide II band), 1413 cm^{-1} C-N stretch, 1224 and 1075 cm^{-1} C-O stretch vibration in urethane structure. The weaker vibration band at *ca.* 1311 cm^{-1} corresponds to the combination between N-H bending vibration and C-N stretching vibration. The peaks at *ca.* 1732 cm^{-1} corres-

ponds to C=O stretching vibrations in ester structure. The absorption peak at *ca.* 1599 cm^{-1} could be attributed to C=C in-plane vibration/stretch in aromatic ring, respectively. The bands at *ca.* 2940 , 2858 and 2796 cm^{-1} can be attributed to asymmetric and symmetric stretching of C-H group.

As can be seen, before exposure, all the 3328 , 1732 and 1700 cm^{-1} bands of M-ETPU coating are broader slightly than that of ETPU film, which can be attributed to O-H and C=O from additives. After exposure to O_3/UV environment, the 3328 cm^{-1} band broadens remarkably, which may reflect hydroperoxide formation¹³ and the concurrent broadening of the 1732 and 1700 cm^{-1} bands suggests the generation of new carbonyl species, which could include the formation of quinine-imides structure (yellow)⁹; the decreasing bands at 1533 and 1075 cm^{-1} could be associated with the scission of the urethane group¹⁴. The substantial decreasing of the 2940 and 2858 cm^{-1} bands indicates significant loss in the methylene group content of the coatings, which may be attributed to hydroperoxidation. After exposure to UV radiation, the 3328 cm^{-1} broadens distinctly and the 1732 and 1700 cm^{-1} bands broaden slightly. After exposure to O_3 atmosphere, all the 3328 cm^{-1} band, the 1732 and 1700 cm^{-1} broaden slightly. Therefore, after same time of exposure, the aging extent of M-ETPU film exposed to O_3/UV environment is much larger than that of M-ETPU film exposed to UV radiation and O_3 atmosphere, respectively.

Yellowness index and synergistic aging effect: Exposure of ETPU and M-ETPU coatings could result in discoloration of the coatings. Therefore yellowness index measurement is a suitable mean for studying the induced chemical changes in these coatings. The changes of yellowness index in both ETPU and M-ETPU coatings are reported in Fig. 3 wherein ' O_3+UV ' represents the arithmetic sum obtained as a result of yellowness index of the coatings after same time of exposure to O_3 environment and to UV radiation in separate case. As can be seen, yellowness index of ETPU and M-ETPU coatings increase slowly with incremental exposure time after 600 h of exposure to O_3 environment and to UV radiation in separate case, which have reached to the values of 14.9 and 10.4 for ETPU coatings, respectively and 9.4 and 9.8 for M-ETPU coatings, respectively. Whereas after exposure to O_3/UV environment, yellowness index of ETPU and M-ETPU coatings increase dramatically with increasing exposure time before 150 h and after that yellowness index of ETPU coating changes slightly, which has reached to the maximum value of 43.7 at 350 h of exposure and yellowness index of M-ETPU almost maintains the maximum value of 34.1 at 350 h of exposure. It can be seen that the yellowing process has almost reached to its equilibrium value during 150 h of exposure to O_3/UV environment and the yellowing process has not reached to its equilibrium value during 600 h of exposure to O_3 environment and to UV radiation in separate case.

In addition, the O_3/UV curve is well above the O_3+UV curve, which means the actual yellowness index of coatings after exposure to O_3/UV environment is much higher than the sum of all of yellowness index of the same coatings after same time of exposure to the same concentration of ozone atmosphere and to the same intensity of UV radiation in separate case. It is suggested that there is dramatic synergistic aging effect between ozone-aging and UV-aging for both ETPU and

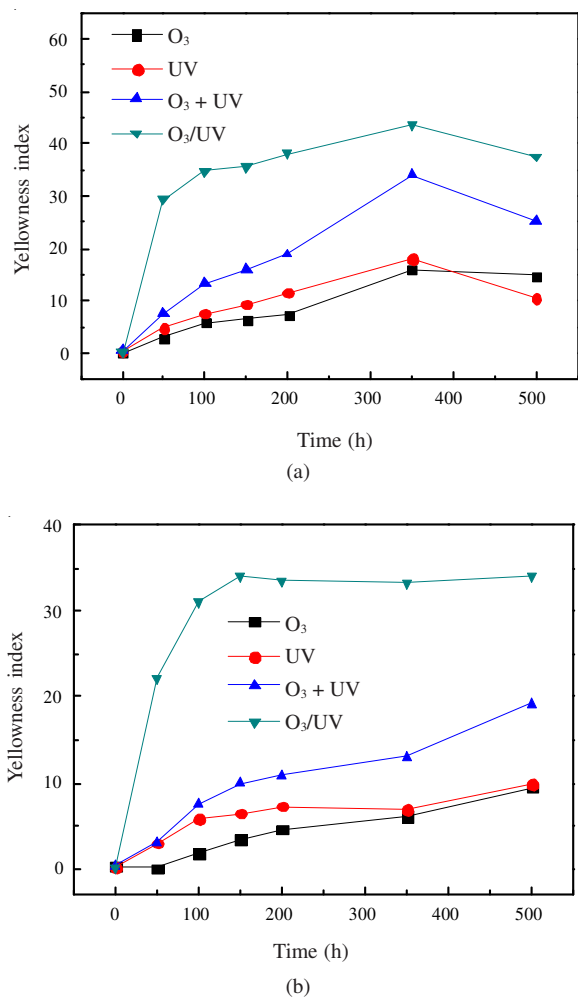


Fig. 3. Changes of yellowness index of the coatings, (a) ETPU; (b) M-ETPU

M-ETPU coatings during 600 h of exposure when yellowness index is used as evaluation index.

The above yellowness index changes can be related to the extreme susceptibility of these systems to yellowing and the quick and extensive extent of yellowing. This yellowing is assumably caused by the degradation reactions in the backbone of the polymer. Exposure to O₃, UV and O₃/UV environment changes physical and chemical characteristics of the coatings surface which results in rapid colour change and degradation, which may involve photo-oxidation of the aromatic functional groups and direct photolytic cleavage of the urethane group producing a diquinone imide⁹. Quinone imide is the chromophore which is responsible for the rapid yellowing of polyurethane. These changes are consistent with the changes of FT-IR spectra.

Fig. 3 shows the adding composite additive decreases yellowness index of M-ETPU coating considerably, which means aging resistance of the composite additive is distinct. This may be related to the following reasons, UV light provides enough energy for ETPU aging and ozone may work as an oxidant for ETPU degradation, which may accelerate the aging process of ETPU.

UV absorbers have the property to convert the energy absorbed from UV light into heat, antioxidant can restrain the formation of free radical and hydroperoxide and HALS has a

protection effect on UV absorber against photolysis. The composite absorbers impart better yellowing resistance as compare to HALS as they absorb UV light and reduce the rate of ETPU degradation at the preliminary stage of weather, where as the HALS may work by scavenging the radicals formed during the ETPU degradation⁸.

Photo-oxidation index and synergistic aging effect: In order to express the aging extent of the coatings after exposure, photo-oxidation index of coatings as a function of exposure time is shown in Fig. 4, wherein 'O₃+UV' represents the arithmetic sum obtained as a result of photo-oxidation index of the coatings after same time of exposure to O₃ environment and to UV radiation in separate case. As can be seen, after exposure to O₃ environment and to UV radiation in separate case, photo-oxidation index of ETPU and M-ETPU coatings increases slowly with increasing exposure time, respectively, for example, photo-oxidation index of ETPU and M-ETPU coatings are 0.890 and 0.818 after 600 h of exposure to O₃, respectively and are 0.949 and 0.597 after 600 h of exposure to UV radiation, respectively. Whereas after exposure to O₃/UV environment, photo-oxidation index of ETPU and M-ETPU coatings increases slowly before 200 h and increases remarkably with increasing exposure time, for example, photo-oxidation index of ETPU and M-ETPU coatings have reached to 25.619 and 14.618 after 600 h of exposure, respectively, which are much higher than that of O₃+UV. It is suggested that synergistic aging effect between ozone-aging and UV-aging is more and more remarkable for both ETPU and M-ETPU coatings after 200 h of exposure when photo-oxidation index is used as evaluation index. In addition, photo-oxidation index of M-ETPU coating is much lower than that of ETPU coating after same time of exposure, which can be attributed to the protection effect of the additives as mentioned above.

Carbonyl index and synergistic aging effect: For a more quantitative expression of the aging extent, carbonyl index of coatings as a function of exposure time is shown in Fig. 5, wherein 'O₃+UV' represents the arithmetic sum obtained as a result of carbonyl index of the coatings after same time of exposure to O₃ environment and to UV radiation in separate case. It is found that both carbonyl index of ETPU and M-ETPU coatings almost maintains between 0.4-0.5 during 600 h of exposure to O₃ environment. After exposure to UV radiation, both carbonyl index of ETPU and M-ETPU coatings increase slowly with increasing exposure time, which are 0.802 and 0.584 after 600 h of exposure, respectively. Whereas after exposure to O₃/UV environment, carbonyl index of ETPU coating almost increases linearly with incremental exposure time, it is more and more higher than that of O₃+UV for ETPU coating after 200 h of exposure; however, carbonyl index of M-ETPU coating first increases slowly before 200 h, which may be related to the protection effect of the additives in M-ETPU coating and then increases rapidly with increasing exposure time, which can be attributed to the additives loss in M-ETPU coating after 200 h of accelerated aging, it is more and more higher than that of O₃+UV for M-ETPU coating after 250 h of exposure. It is suggested that the synergistic aging effect between ozone-aging and UV-aging is more and more remarkable for ETPU and M-ETPU coatings after 250 h of exposure when carbonyl index is used as evaluation index.

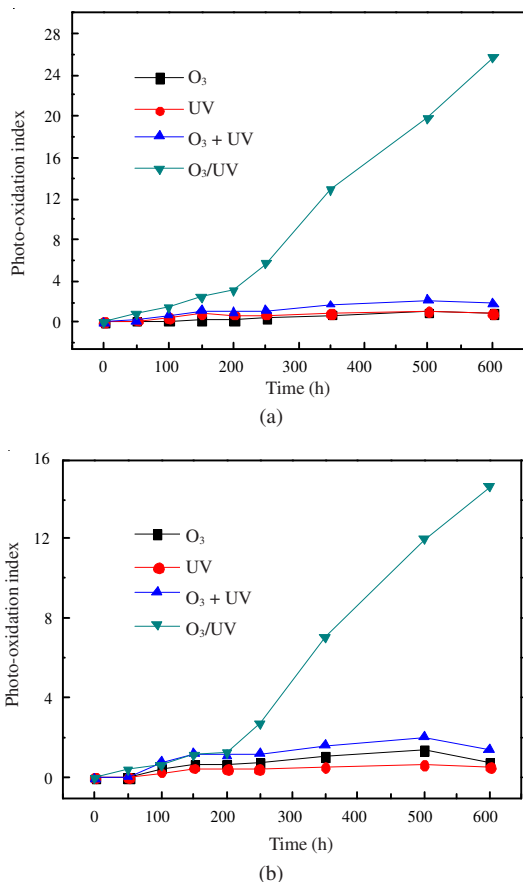


Fig. 4. Photo-oxidation index of the coatings as a function of exposure time, (a) ETPU; (b) M-ETPU

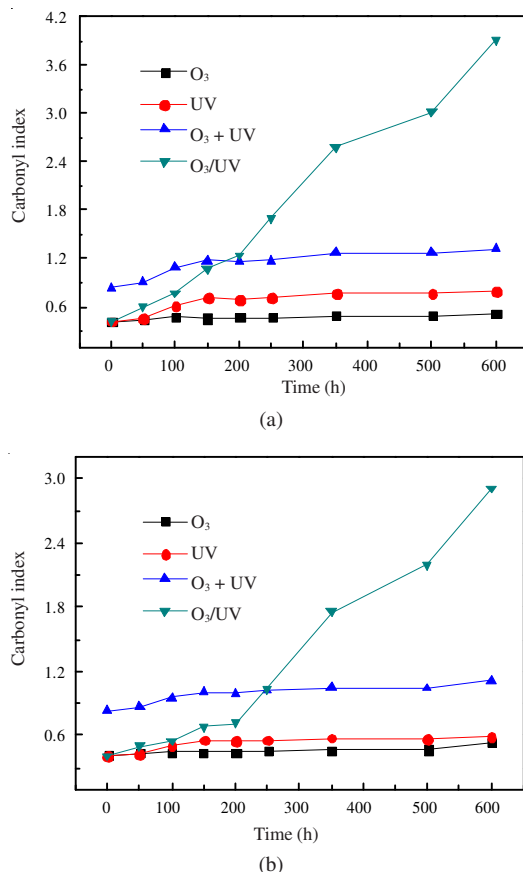


Fig. 5. Carbonyl index of the coatings as a function of exposure time, (a) ETPU; (b) M-ETPU

Conclusion

The ozone and ultraviolet initiate autoxidation of urethane bridge in the ETPU chain to quinone-imide structure and trigger formation of hydroperoxides and new carbonyl species. However, the aging extent of M-ETPU was significantly reduced. Yellowness index of the coatings increases dramatically with incremental exposure time, there is distinct synergistic aging effect between ozone-aging and UV-aging when yellowness index is used as evaluation index. After 200 h of exposure, photo-oxidation index of the coatings increases remarkably with increasing exposure time, synergistic aging effect between ozone-aging and UV-aging is more and more remarkable when photo-oxidation index is used as evaluation index. After 250 h of exposure, carbonyl index of the coatings also shows significant synergistic aging effect between ozone-aging and UV-aging is more and more remarkable when carbonyl index is used as evaluation index.

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