



Effect of Composite Additives on Weather-Resistance Properties of Polyurethane Films

Y.Z. WANG*, Z.H. SUN, H.Y. WANG*, K.S. TIAN and H.C. WANG

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

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

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Weather-resistance effect of two organic ultraviolet (UV) absorbers of UV-531 and UV-327 on thermo-plastic polyether polyurethane films exposed to constant UV radiation with ozone atmosphere was studied by using a self-designed aging device. The changes of the structures and the properties of the polyurethane films during UV/O₃ aging were measured by colorimeter apparatus, FT-IR spectroscopy and UV-visible spectroscopy. The results show that UV-531 and the composite UV absorbers could inhibit yellowing of the polyurethane films. The UV resistance properties of the polyurethane films are distinctly improved by adding the composite UV absorbers to the matrix. UV-327 could inhibit effectively photodegradation of the polyurethane films. During photodegradation of the polyurethane films modified by the composite UV absorbers, neither distinct synergism nor distinct antagonism is observed.

Keywords: Polyurethane films, Composite additive, Accelerated aging, Synergistic effect.

INTRODUCTION

Polyurethane elastomers, consisting of alternating soft and hard segments have a wide range of properties including abrasion resistance, oil resistance, tear resistance, chemical resistance, good adhesion with other materials, high-flexibility and vibration absorption ability. Therefore, they have been widely used in industrial production and daily life¹.

In the storage and use, polyurethane materials are subjected to various environmental factors such as solar radiation, heat, air and water, leading to the degradation of polyurethane including discoloration, brittleness and degradation of mechanical properties which result in a loss of the value in use². Thus, it is an important work to slow down the aging process and to extend the service life of polyurethane. Two ways are used to extend the service life of polyurethane, one is to modify the structure of the polyurethane molecules and another is to add UV stabilizers to the polyurethane³⁻⁶.

Organic UV absorbers are a class of polymers absorbing a particular band ultraviolet and play an important role in improving weather-resistance of polyurethanes. Many different types of organic UV absorbers are widely used in the industry due to their selectivity characteristics and light resistance properties.

Benzophenone and benzotriazole are the main types of organic UV absorbers. UV-531 is a benzophenone-type UV absorber which has the characteristic absorption at wavelengths

below 350 nm and UV-327 is a benzotriazole-type UV absorber which has a strong absorption in the wavelength range of 350-380 nm. It is reported⁷ that benzotriazole UV absorbers are more sensitive to UV radiation than that of benzophenone UV absorbers and benzotriazole UV absorbers have a stronger absorption than that of benzophenone UV absorbers in the early stage of UV aging. However, UV absorption effects of benzophenone UV absorbers are more and more notable with increasing aging time. Therefore, the distinct weather-resistance effects on the polyurethanes exposed to UV radiation may be observed when UV-531 and UV-327 are used together.

The high-altitude airship and balloon are continuously exposed to stratospheric environment throughout their service life. High environmental resistance is necessary for the polyurethane films, 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 the polyurethane films. In this work, two organic UV absorbers of UV-531 and UV-327 were added to thermo-plastic polyether polyurethane in the separate and complex ways, respectively and the modified polyurethane films were obtained. Then the accelerated weathering test for the modified polyurethane films exposed to constant UV radiation with O₃ atmosphere was performed to study the weather-resistance properties of the polyurethane films. It is also discussed whether there is synergism or antagonism between UV-531 and UV-327 during O₃/UV aging.

EXPERIMENTAL

Polyether polyurethane pellets (I180 A, BASF), ultraviolet absorbent UV-327 (no less than 99 wt. %, Nanjing Hua Lim Chemical Co., Ltd.), ultraviolet absorbent UV-531 (no less than 99.0 wt. %, Shanghai De Yud Trading Co., Ltd.), N,N-dimethyl formamide (DMF) (AR, Tianjin Kay Tong Chemical Reagent Co., Ltd.), 1,4-butane diol (AR., Tianjin Sailboats Chemical Reagent Technology Co., Ltd.).

Experimental device: The self-designed aging device includes the following parts: AD-XF-5 P ozone machine (ozone concentration range of 0-1000 ppm, Jinan Jie Anritsu Technology Co., Ltd.), ACO-318 electromagnetic air compressor (Guangdong Haili Group Limited), UVB-313 ultraviolet radiation meter (Photoelectric Instrument Factory Beijing Normal University), UVB-313 fluorescent UV lamp (U.S. Q-Lab Corporation), CPR-G 6 ozone detection probe (Beijing Mountain Water Environmental Technologies Ltd.), FA 2004 electronic balance (Shanghai Shun Yuheng Ping Scientific Instrument Co.), JFA-II coating machine (Shanghai Modern Environmental Engineering Technology Co., Ltd.), DZF vacuum oven (Shanghai Jing Hong Test Equipment Co., Ltd.).

Specimen preparation: The additives in Table-1 were separately dissolved in a mixed solvent of DMF/butanone (70:20, w:w). 10 wt. % polyurethane pellets were gradually added to the mixed solvent until the additives were uniformly dispersed. The mixture was stirred at 60 °C for 2 h, until the slurry of 12-13 wt. % solids content was obtained.

Sample	UV327 (wt. %)	UV531 (wt. %)
PU	0	0
PU-UV327	0.25	0
PU-UV531	0	0.25
PU-COM	0.25	0.25

The slurry was drawn out on the CaF₂ sheets in the coating machine at 2000 rpm for 5 s and the obtained products were dried for 12 h at 50 °C under vacuum.

Aging experiments: The accelerated weathering tests for the polyurethane films exposed to constant UV radiation with O₃ atmosphere were performed by using the self-designed aging device. The experimental conditions during the accelerated aging were the UV irradiation intensity of (400 ± 20) μW/cm², the ozone concentration of (100 ± 2) ppm, the temperature of 25 °C and the relative humidity of 10 %. The samples were taken out after 20, 60, 120, 160 and 200 h exposure, testing the colour difference, yellowness index, FT-IR spectra and UV-visible spectra.

Properties characterization: The colour difference and yellowness index were measured using a CR-10 colorimeter (Konica Minolta Corporation, Japan). FT-IR spectra were recorded using a Nicolet is 10 infrared spectrometer (Thermo Fisher Scientific), scanning range of 4000-400 cm⁻¹. UV-visible spectra in the range of 190-800 nm were obtained using a UV-2550 UV-visible spectrophotometer (Shimadzu Corporation, Japan).

RESULTS AND DISCUSSION

Colour difference and yellowness index: The variations of colour difference and yellowness index of PU, PU-UV327, PU-UV531 and PU-COM films with exposure time are shown in Figs. 1 and 2, respectively, where calculated values are obtained according to the composite ratio of UV-531 and UV-327 in PU-COM films and the measured values of PU-UV327 and PU-UV531 films.

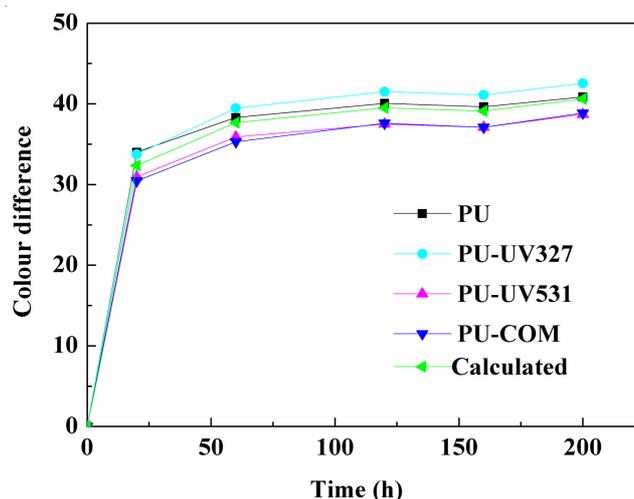


Fig. 1. Variation of colour difference as a function of exposure time

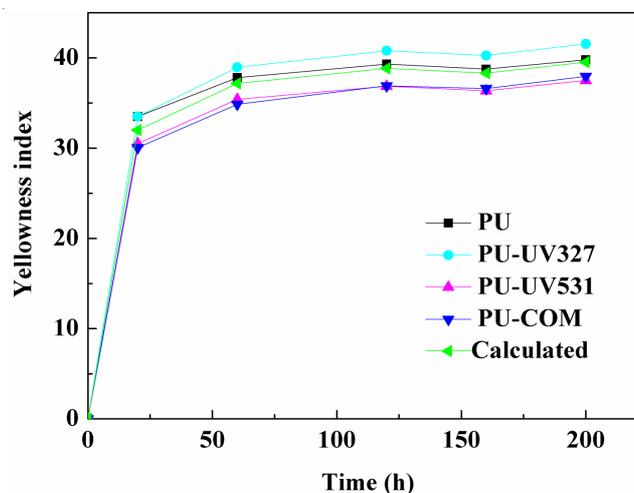


Fig. 2. Variation of yellowness index as a function of exposure time

Fig. 1 shows that the change rule of colour differences of the various polyurethane films is basically consistent. The changes are notable during initial 20 h of aging, while the changes are slowly after 60 h of continuous aging. At the same aging time, the colour differences of PU-UV531 and PU-COM films are significantly lower than that of polyurethane films and the colour difference of PU-UV327 films is slightly higher than that of polyurethane films. The results indicate that UV-531 and composite ultraviolet absorbers are effective in preventing discoloration for the polyether polyurethane films.

Fig. 2 shows that the change rule of the yellowness indexes is basically consistent with that of colour differences for the various films. The results illuminate that UV-531 and composite

ultraviolet absorbers are effective in inhibiting yellowing of the polyether polyurethane films, which suggests that UV radiation induces the chain scission reactions of the polyurethane molecules, while strong oxidative properties of the ozone intensify the aging reactions in the UV/O₃ environment, or in active ozone, or in the presence of UV light and could produce a large number of active oxygen atoms to act on the reactive sites of polymer chains, resulting in the acceleration of reactions and the generation of a large number of the chromophores and auxochromes⁸⁻¹¹.

The calculated values of colour difference and yellowness index are significantly higher than the measured values of them at the same exposure time. This indicates that synergistic effect on yellowing resistance of the polyurethane films exist when a combination of UV-531 and UV-327 is added to the matrix, which may be related to the strong UV absorption of the composite UV absorbers in a wide range of 300-380 nm⁷.

UV-visible spectroscopy: The UV-visible spectra of polyurethane, PU-UV327, PU-UV531 and PU-COM films during exposure time are shown in Fig. 3. It can be seen that polyurethane films have little UV absorption at 300-400 nm range before aging. UV absorption band of PU-UV327 films and PU-UV531 films appear in the wavelength range of 300-380 and 300-350 nm, respectively. The strong UV absorption band of PU-COM films is observed in the range of 300-380 nm, which may be attributed to the following reasons: UV-327 can strongly absorb UV radiation in the wavelength range of 200-380 nm, while UV-531 mainly absorbs UV radiation at wavelengths below 350 nm. When UV-531 and UV-327 were used together, the films show a significant UV absorption in a wide range of 300-380 nm, especially in the 300-350 nm region. The absorption peaks with maximum intensity near 200 nm are commonly ascribed to the $n-\pi^*$ transition from carbonyl groups¹². UV absorbance near 200 nm gradually increases and the peak gradually widens at prolonged aging, which indicates that the generated carbonyl compounds are increasing and the types are continuously changing in the aging process. The growth rate of UV absorbance of PU-UV327 films near 200 nm is slower than that of polyurethane films and the peak width is narrower than that of polyurethane films¹³, indicating the reduction of the number and the types of carbonyl compounds due to the addition of UV-327. The growth rate of UV absorbance of PU-UV531 films near 200 nm is faster than that of polyurethane films and the peak width is wider than that of polyurethane films, which indicates that the number and the types of carbonyl compounds are increased due to the addition of UV-531 in the aging process. Compared with the peaks of unexposed films, UV absorption peaks of the aged films show a bathochromic shift, which could be ascribed to the formation and development of quinone-imide chromophore structures during the degradation^{14,15}. Fig. 3 also shows that after same time of exposure, the extent of bathochromic shift of UV absorption peaks of PU-UV531 and PU-COM films is significantly less than that of PU films, while the UV absorption peaks of PU-UV327 films is wider than that of PU films. The effectiveness of UV-531 and composite UV absorbers is evident in UV-resistance and yellowing-resistance during UV/O₃ exposure of polyurethane film. However, the addition of UV-327

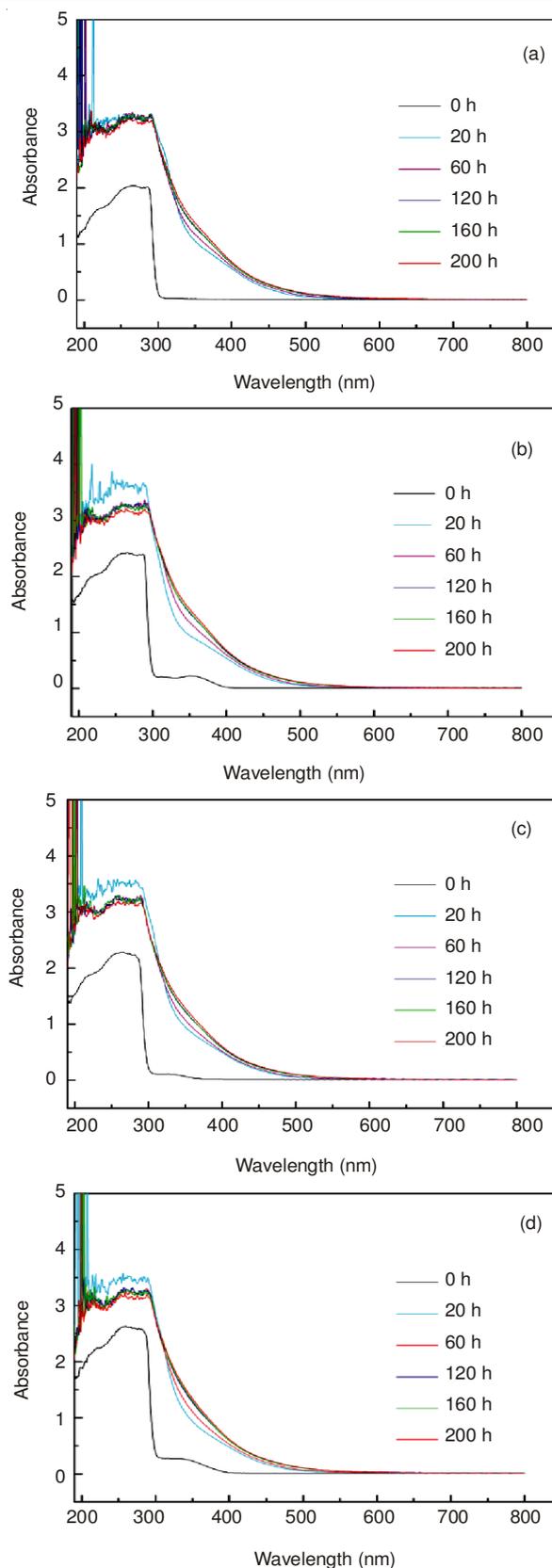


Fig. 3. Variation of UV-visible spectra as a function of exposure time: (a) PU; (b) PU-UV327; (c) PU-UV531; (d) PU-COM

exacerbates yellowing-resistance properties of the films. The conclusions are basically consistent with the results of colour difference and yellowness index.

Infrared spectroscopy: The change of transmission in the FT-IR spectra of polyurethane, PU-UV327, PU-UV531 and PU-COM films at different exposure times are given in Fig. 4a-d. The assignments of the bands are performed according

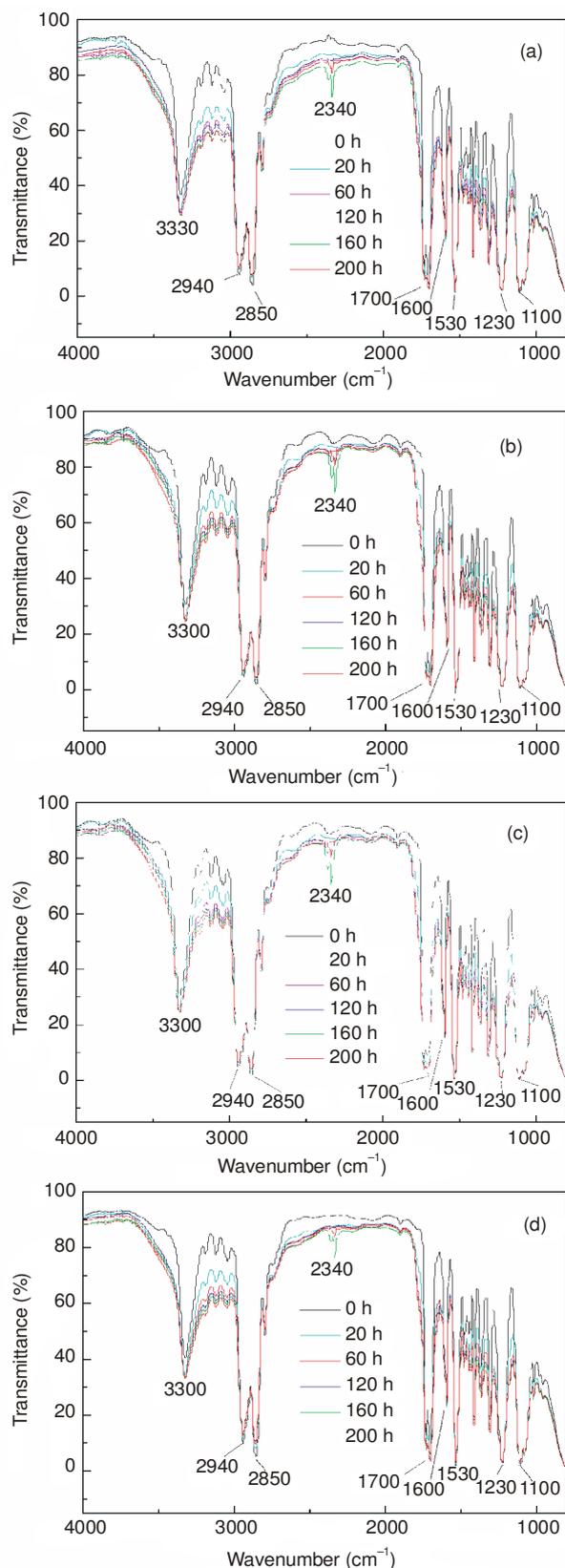


Fig. 4. Variation of FT-IR spectra as a function of exposure time: (a) PU; (b) PU-UV327; (c) PU-UV531; (d) PU-COM

to the literature of FT-IR data for polyurethane system¹⁶⁻¹⁸. It can be seen that the internal structures of the polyurethane films have been changed greatly after aging. The formation of hydroxyl groups could explain the increase in the intensity of the bands in the region of 3500-3200 cm⁻¹ ascribed to -NH/-OH stretching vibration. The several strong peaks in the 3020-2750 cm⁻¹ region assigned to -CH₃ symmetric and asymmetric stretching peaks are almost constant after aging. The appearance of absorption bands of low relative intensity at 2340 cm⁻¹ is likely arising from the -NCO asymmetric stretching absorption in the aging process¹⁹. The increase in absorption in the carbonyl region (1763-1640 cm⁻¹) for the various polyurethane coating suggests the formation of new oxidized groups as a result of photochemical reactions¹⁷. The intensity loss of the narrow strong absorption at 1230 cm⁻¹ ascribed to -C-C stretching peak indicates that the cleavage of carbon bond may have occurred. The narrow strong peak at 1530 cm⁻¹ is assigned to the coupling peak of -NH bending and -CN stretching motion. -C-O absorption peak (1110 cm⁻¹) and -CN stretching peak in the urethane have a slight decrease after aging, which indicates the cleavage of -C-O and -CN bonds and the formation of -C=O, -NH and -OH bonds in a molecule during the aging process. This may be related to the growth of quinone-imide groups²⁰⁻²³.

Photooxidation index and carbonyl index: The degree of polyurethane photooxidation is usually characterized by photooxidation index (PI) and carbonyl index (CI) according to the formula (1) and (2):

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

$$CI = C_{-C=O} / B_{-CH_3} \quad (2)$$

wherein, A represents -OH and -NH peak area; B and C represent -CH₃ and -C=O peak area, respectively.

The variations of photo oxidation index and carbonyl index of polyurethane, PU-UV327, PU-UV531 and PU-COM films as a function of exposure time are shown in Figs. 5 and 6, respectively. It can be seen that photooxidation index and carbonyl index of the various films increase gradually with the aging time and the increase rates of photooxidation index and carbonyl index of PU-UV327 films are significantly faster than that of the other films. This indicates UV-327 could inhibit the photodegradation of the films effectively and reduce the formation rate of carbonyl compounds in the UV/O₃ environment. This conclusion is basically consistent with that of UV-visible spectrum. The photostabilization mechanisms of UV-327 and UV-531 are substantially same, which is attributed to the presence of a strong intramolecular hydrogen bond between the *o*-hydroxyl group of the phenyl ring and the nitrogen atom in molecular structure. This hydrogen bond allows the energy absorbed by the molecule to be dissipated harmlessly as heat, thereby protecting the material²⁴. However, the photooxidation rate of the films and the number and the types of carbonyl compounds are increased as a result of the addition of UV-531, which may be related to the poor light stability of UV-531.

It can also be seen that the calculated value and the measured value of photooxidation index and carbonyl index

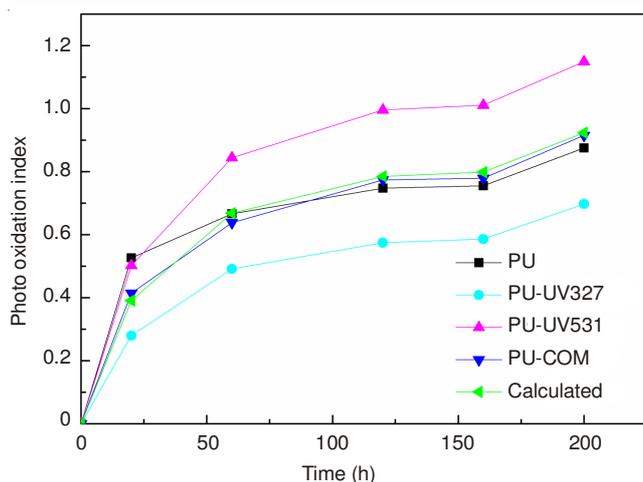


Fig. 5. Variation of photooxidation index as a function of exposure time

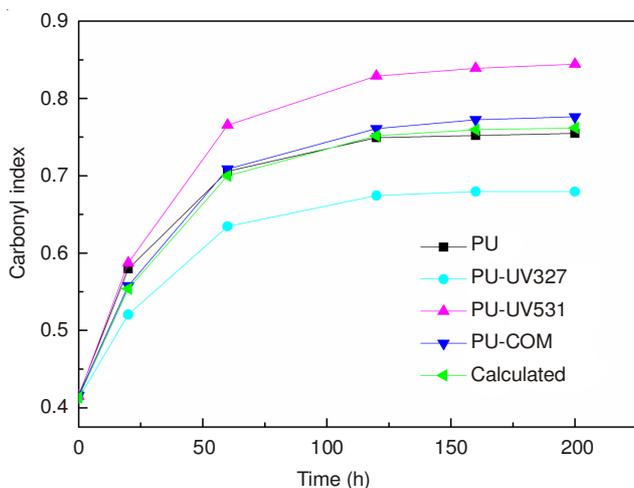


Fig. 6. Variation of carbonyl index as a function of exposure time

for PU-COM films are basically consistent. This indicates that neither distinct synergism nor distinct antagonism exists during the photodegradation of the polyurethane films modified by the composite ultraviolet absorbers.

Conclusions

- UV-531 and the composite UV absorbers could effectively inhibit yellowing of the polyether polyurethane films.

- During exposure to UV/O₃ environment, the addition of UV-531 and the composite UV absorbers can distinctly improve the UV aging-resistance properties of the polyurethane films.

- UV-327 could effectively inhibit the photodegradation of the polyurethane films. Neither distinct synergism nor distinct antagonism is observed during photodegradation of the polyurethane films modified by the composite UV absorbers.

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