

Research Article

O₃/UV Synergistic Aging of Polyester Polyurethane Film Modified by Composite UV Absorber

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Received 30 March 2013; Revised 12 May 2013; Accepted 26 May 2013

Academic Editor: Lavinia Balan

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The pure polyester polyurethane (TPU) film and the modified TPU (M-TPU) film containing 2.0 wt.% inorganic UV absorbers mixture (nano-ZnO/CeO₂ with weight ratio of 3:2) and 0.5 wt.% organic UV absorbers mixture (UV-531/UV-327 with weight ratio of 1:1) were prepared by spin-coating technique. The accelerated aging tests of the films exposed to constant UV radiation of $400 \pm 20 \mu\text{W}/\text{cm}^2$ (313 nm) with an ozone atmosphere of 100 ± 2 ppm were carried out by using a self-designed aging equipment at ambient temperature and relative humidity of 20%. The aging resistance properties of the films were evaluated by UV-Vis spectra, Fourier transform infrared spectra (FT-IR), photooxidation index, and carbonyl index analysis. The results show that the composite UV absorber has better protection for TPU system, which reduces distinctly the degradation of TPU film. O₃/UV aging of the films increases with incremental exposure time. PI and CI of TPU and M-TPU films increase with increasing exposure time, respectively. PI and CI of M-TPU films are much lower than that of TPU film after the same time of exposure, respectively. Distinct synergistic aging effect exists between ozone aging and UV aging when PI and CI are used as evaluation index, respectively. Of course, the formula of these additives needs further improvement for industrial application.

1. Introduction

It is well known that exposure of polymer materials to an aggressive environments (i.e., UV radiation, thermal exposure, and oxidative atmosphere) causes changes in their physical and chemical characteristics [1]. The thermoplastic polyurethane material 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 plastics, glass fibers, wood, the aircraft industry, stratospheric airship, and so forth, [2–4]. However, TPU material is susceptible to degradation, which would lead to discoloration and even total destruction. Therefore, its use in outdoor applications is limited. It is very important to impart light stability to the TPU films by adding additives into matrix [5]. UV absorbers (UVAs) work by absorbing ultraviolet light that could otherwise initiate photooxidation. However, the main drawback of organic UVAs is their relative high loss rate due to continuous

conversion to radicals. Moreover, organic UVAs have certain absorption peaks in narrow UV ranges; while inorganic UVAs have relatively wide absorption regions. Recently inorganic nanoparticles such as zinc oxide [6] and cerium Oxide [7] were used as efficient UVAs. Moreover, the combination of different additives and/or their mixtures could have a positive synergistic effect on the photostabilization of polymers.

Since the protection films of high-altitude airship are continuously exposed to stratospheric environment throughout their service life, the airship films material must also be designed to resist the harsh stratospheric environment such as high ozone concentration and intense UV. Well aging resistance is necessary for the application of TPU material to airship film. It is important to understand the ultraviolet and ozone-aging-induced degradation processes of TPU film. The purpose of this study was to investigate the aging behavior of TPU material with and without composite additives exposed to UV with O₃ environment. The composite UV absorber is composed of a mixture of ZnO and CeO₂ and a mixture of

UV-327 and UV-531. The investigation has not been reported up till now.

2. Materials and Methods

2.1. Materials. The pure TPU material (B85A) was of commercial grade from BASF Company. The zinc oxide and the ceria nanoparticles used in this work were supplied by Nanjing High Technology of Nano Co., Ltd., China. The nano-zinc oxide was surface treated with an organosilane coupling agent of γ -methacryloxypropyltrimethoxysilane (KH-570) in the supplied form. Organic UV absorbers of UV-327 (namely, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole) and UV-531 (namely, 2-hydroxy-4-octyloxybenzophenone) used in this work were supplied by Nanjing Hua Lim Chemical Co., Ltd., China.

2.2. Surface Modification of the Ceria Nanoparticles. The ceria nanoparticles were modified with an organosilane coupling agent of KH-570. The main procedure was as follows: 5 g of the predried ceria nanoparticles and 100 mL of the solvent mixture (ethanol/water with volume ratio of 3:1) was poured into a three-neck flask of 250 mL and dispersed by ultrasonic irradiating for 30 min at room temperature; 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 for 4 h under magnetic stirring at 85°C; modified nanoparticles were then filtered under suction, and physically adsorbed KH-570 compounds were soxhlet extracted with ethanol for 24 h, and were finally dried at 80°C in a vacuum oven for 12 h.

2.3. Preparation of Films. Calcium fluoride (CaF₂) discs with a diameter of 25 mm and a thickness of 2 mm were selected as the substrate for the exposure study because they have excellent moisture and heat resistance properties and is transparent to both UV and infrared radiation [8, 9], allowing for periodic characterization of spectral UV-visible and infrared radiation. The polyester polyurethane (TPU) film (represented as TPU hereafter) and the modified TPU film (represented as M-TPU hereafter) containing 2.0 wt.% inorganic UV absorbers mixture (nano-ZnO/CeO₂ with weight ratio of 3:2) and 0.5 wt.% organic UV absorbers mixture (UV-531/UV-327 with weight ratio of 1:1) were prepared by spin-coating technique. For the first step, nano-zinc oxide and nano-ceria modified with an organosilane coupling agent were heated at 80°C in a vacuum oven for 12 h to remove adsorbed moisture; the required UV absorbers were directly added to the solvent mixture (DMF/butanone with volume ratio of 7:2) and dispersed by ultrasonic irradiating for 30 min. This step was followed by the slow addition of the stoichiometric amount TPU 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 dispersion of TPU material had a solid content of 15% ± 2%. Subsequently, the composite was degassed, flooded onto the substrates, and spun at 2000 rpm for 10 sec. The films were then cured at 60°C for 12 h.

2.4. Accelerated Aging Tests. Accelerated aging tests for TPU and M-TPU films were carried out by using a self-designed equipment, in which the intensity of UV and concentration of ozone can be well controlled, respectively. The source of UV radiation was fluorescent ultraviolet tube (UVB-313EL type). According to test procedure, the films were continuously exposed to constant UV radiation of 400 ± 20 μW/cm² (313 nm) with an ozone atmosphere of 100 ± 2 ppm (represented as O₃/UV hereafter) at ambient temperature and relative humidity of 20% for different time spans with maximum exposure time of 200 h, respectively. Each film was taken out after 20 h, 60 h, 120 h, 160 h, and 200 h of exposure for monitoring the degradation of the composite films by UV-visible spectra, FT-IR spectra, the photooxidation index, and the carbonyl index of the films.

2.5. Characterization and Measurements. UV-visible spectra of TPU and M-TPU films and its changes during exposure were measured by using UV-2550 (Shimadzu Co., Japan) spectrophotometer in the range of 200–800 nm at 0.5 nm increments. FT-IR spectra were recorded by using Nicolet iS10 (Thermo Fisher Scientific Co., USA) spectrometer, and the spectra were recorded in the range of 400–4000 cm⁻¹ with 4 cm⁻¹ resolution and averaging 16 scans. The surface micrograph of the films was observed using S-4800 field-emission scanning electron microscope.

According to FT-IR absorption spectra, the photooxidation index (PI) and the carbonyl index (CI) were calculated by (1) and (2), respectively, as follows:

$$PI = \left(\frac{A_{-\text{OH},-\text{NH}}}{A_{-\text{CH}_3}} \right)_{\text{aged}} - \left(\frac{A_{-\text{OH},-\text{NH}}}{A_{-\text{CH}_3}} \right)_{\text{initial}}, \quad (1)$$

$$CI = \frac{A_{-\text{C}=\text{O}}}{A_{-\text{CH}_3}}, \quad (2)$$

wherein $A_{-\text{OH},-\text{NH}}$ is the area of the absorption band associated with -OH, -NH group and $A_{-\text{CH}_3}$ is the area of the absorption band attributed to the C-H stretching band. The reference band will not be considerably affected by photooxidation. $A_{-\text{C}=\text{O}}$ is the area of the carbonyl absorption band.

3. Results and Discussion

3.1. Additives Characterization. Figure 1 shows the TEM image of silanized nanoparticles. It can be observed that the particles of ZnO and CeO₂ are in nanometer scale and are mostly of elongated shape. In addition, some irregular shaped ZnO particles can also be found.

The UV absorbance curves of the additives are shown in Figure 2. It shows that an absorption peak at 259 nm for CeO₂ nanoparticles, and there is very high UV absorbance in 200–250 nm and there are two absorption peaks in 270–370 nm for ZnO nanoparticles. It also shows that UV light below approximately 350 nm can be efficiently absorbed by UV absorbers of UV-531, and UV light in 200–250 nm and in 280–380 nm can be efficiently absorbed by UV absorbers of UV-327. It can be deduced that there is very high UV absorbance for

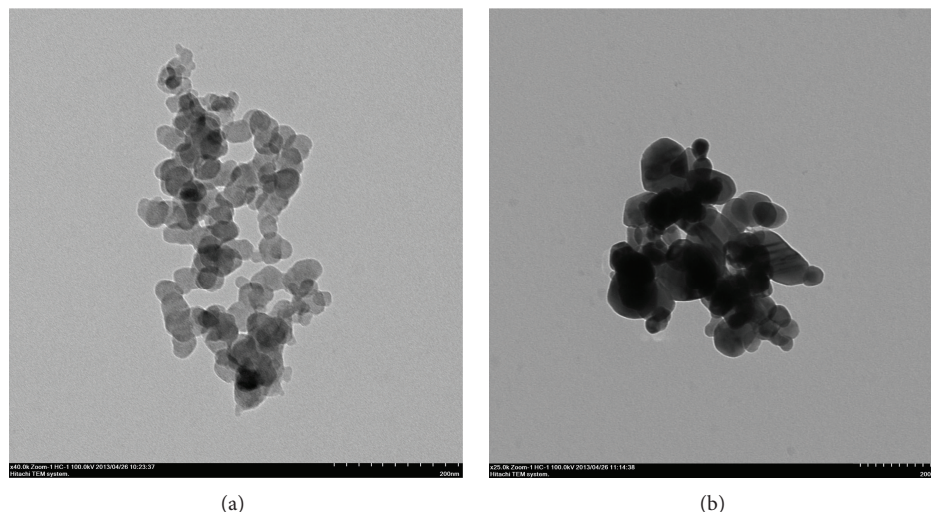


FIGURE 1: TEM image of silanized CeO_2 (a) and ZnO (b) nanoparticles.

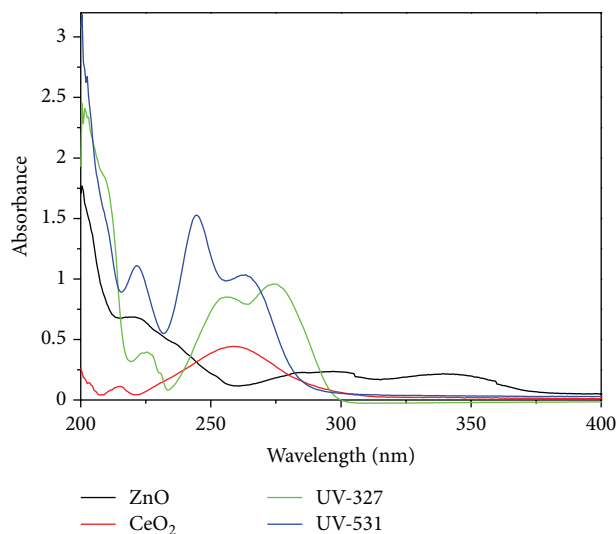


FIGURE 2: UV absorbance curves of the additives.

the composite UV absorber containing 2.0 wt.% inorganic UV absorbers mixture (nano- ZnO/CeO_2 with weight ratio of 3:2) and 0.5 wt.% organic UV absorbers mixture (UV-531/UV-327 with weight ratio of 1:1).

3.2. SEM Micrograph of Film. Figure 3 shows the SEM surface micrograph of TPU and M-TPU films before and after 200 h of UV/ O_3 exposure. Compared with Figures 3(a) and 3(c), the nano- ZnO and nano- CeO_2 particles are well dispersed in M-TPU film. While most of the particles are present as single particle, a certain degree of nanoparticles aggregation can also be found in the image. As can be seen from Figures 3(b) and 3(d), surface cracks are formed in TPU film, while no crack could be seen in M-TPU film after 400 h of UV/ O_3 exposure. The formation of these cracks could be an evidence for the concentration of degradation-induced stresses in specific places of the film. As composite UV absorber absorbs UV light, it reduces the UV intensity at the higher depth of the

film and therefore reduces the probability of stress generation in the film bulk. In this way, composite UV absorber could help the polymeric matrix of the films to remain intact for a longer period of time, and the presence of composite UV absorber in M-TPU film has caused a more uniform degradation of polyurethane.

3.3. UV-Vis Spectra. Figure 4 presents UV-Vis absorption spectra of TPU and M-TPU films exposed to O_3/UV environment as function of exposure time. As shown in Figure 4(a), before exposure, the absorbance curve of TPU film only shows an absorption peak in the region of 200–290 nm. As can be seen from Figure 4(b), there are an absorption peak in the region of 200–290 nm and a broad absorption band in the region of 299–390 nm for M-TPU film. According to Figures 2(a) and 2(b), the absorption peak in the region of 200–290 nm probably originates from composite absorption of ZnO and CeO_2 nanoparticles and UV absorbers of UV-327 and UV-531, and the absorption band in the UV region of 299–390 nm probably originates from composite absorption of ZnO nanoparticles and UV absorbers of UV-327 and UV-531. Therefore, the UV-aging resistance performance of M-TPU film is far superior to that of TPU film.

As can be seen, the absorptions in the region of 200–500 nm (Figure 4(a) for TPU film) and in the region of 200–550 nm (Figure 4(b) for M-TPU film) increase with incremental exposure time. It is reported that incident radiation in the range of 290–450 nm activates a urethane in an autoxidation process [10]. All films absorb relatively substantially more at 390–430 nm than at 565–750 nm and should be more yellow. Additionally, the absorption in the region of 270–310 nm increases with incremental exposure time before 120 h for TPU and M-TPU films, and the simultaneous growth in absorption in the region of 270–310 nm is considered as evidence of the formation of a quinoid structure. These spectral changes suggest that the aromatic structures were oxidized in the central methylene group, leading to highly conjugated quinone products [10, 11]. In addition, visible absorption

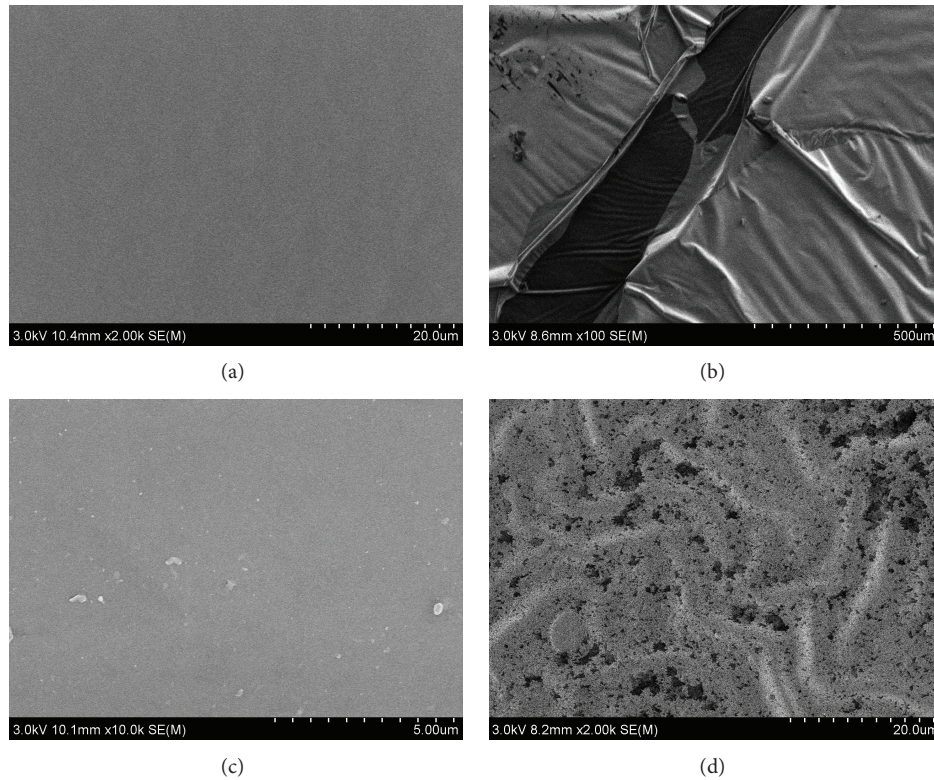


FIGURE 3: SEM micrograph of the film surface: (a) unexposed TPU film; (b) TPU film after 400 h of UV/O₃ exposure; (c) unexposed M-TPU film; (d) M-TPU film after 400 h of UV/O₃ exposure.

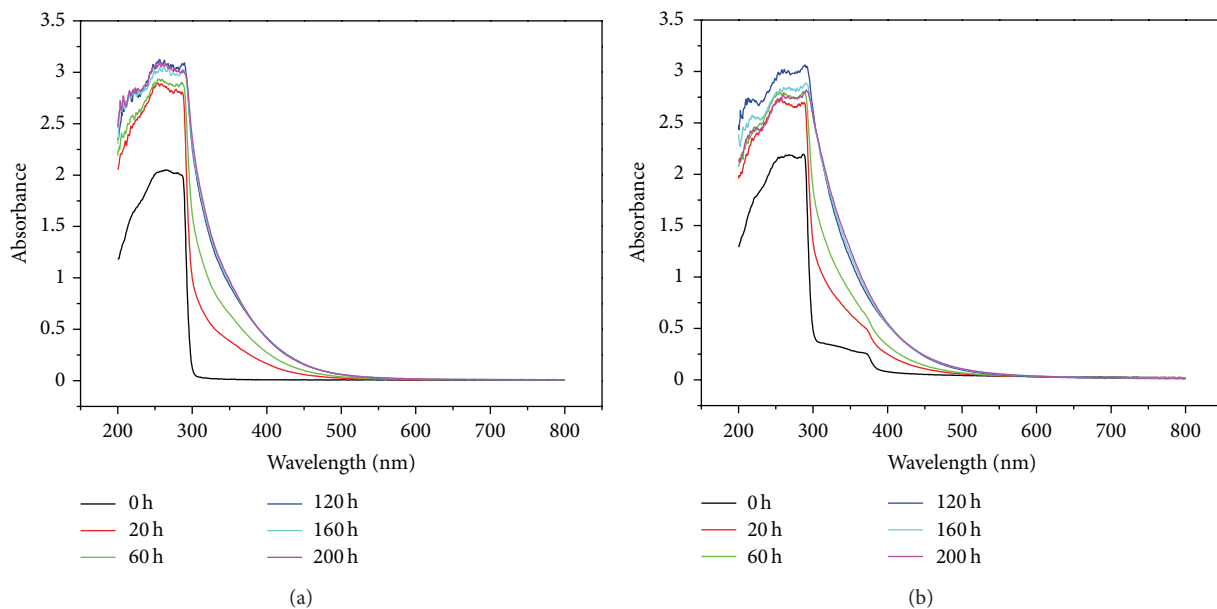


FIGURE 4: UV-Vis spectra of TPU and M-TPU films as function of exposure time, (a) TPU; (b) M-TPU.

spectra of exposed films compared with the spectra of unexposed films show a bathochromic shift (Figures 4(a) and 4(b)). This could be explained by the formation and development of new chromophores, for example, quinoid structures,

polyene sequences, and azo structures [12]. UV-Vis absorption spectra of the unexposed films mean that UV-aging resistance characteristic of M-TPU film is distinctly superior to that of TPU film. This should be attributed to the composite

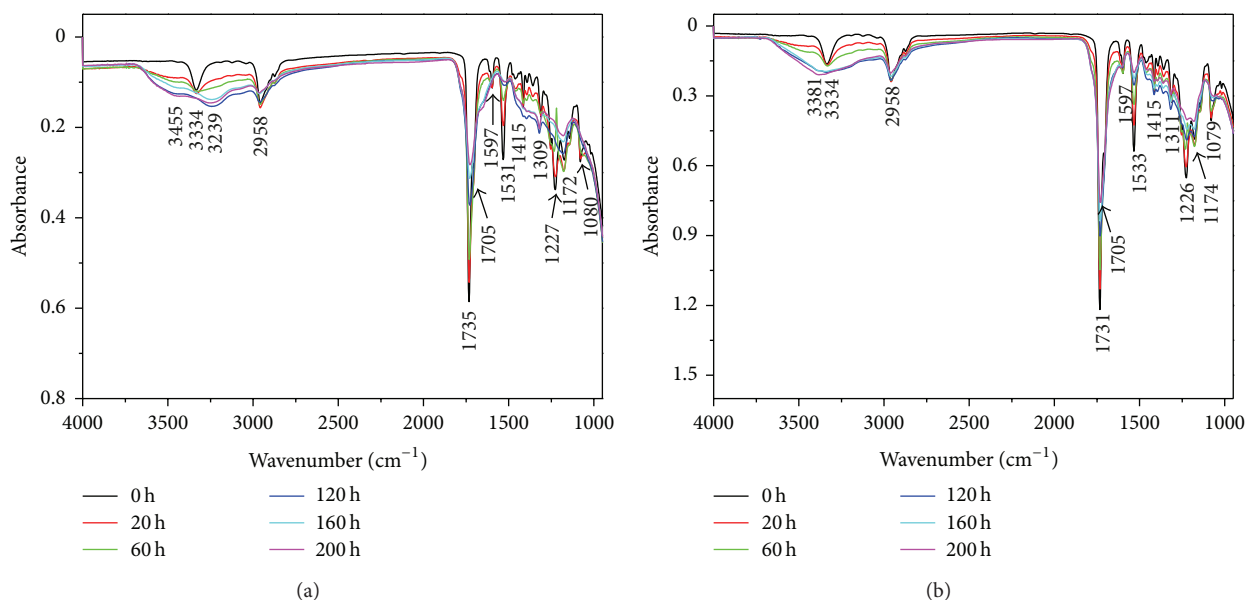


FIGURE 5: FT-IR spectra of TPU and M-TPU films as function of exposure time (a) TPU; (b) M-TPU.

protection effect of the inorganic UV absorbers and organic UV absorbers in M-TPU film.

3.4. FT-IR Spectra. FT-IR spectra of TPU and M-TPU films exposed to O_3 /UV environment as function of exposure time are shown in Figure 5. As can be seen, the absorption peaks between 3700 and 3000 cm^{-1} characterize N–H and O–H stretch vibrations. The peak at ca. 1735 cm^{-1} characterizes C=O stretching vibration in ester structure, while the peak at ca. 1705 cm^{-1} corresponds to C=O stretching vibration in the urethane bond (amide I band), 1533 cm^{-1} N–H deformation (amide II band), and 1413 cm^{-1} C–N stretching. The region of 1300 – 1100 cm^{-1} is characteristic to 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. The absorption band between 3000 and 2800 cm^{-1} can be attributed to the C–H stretching.

As shown in Figure 5, After exposure to O_3 /UV environment, the N–H and O–H bands broaden remarkably with increasing exposure time, which may reflect hydroperoxide formation [13], and the C=O bands broaden gradually with incremental exposure time. This suggests the generation of new carbonyl species, which could include the formation of quinine-imides structure (yellow) [14]; the decline of bands at ca. 1533 and ca. 1079 cm^{-1} could be associated with the scission of the urethane group [15]. The substantial decline of the C–H bands of TPU film indicates significant loss in the methylene group content of the film, which may be attributed to hydroperoxidation, whereas the C–H band of M-TPU film almost remains unchanged, this means that M-TPU film has better aging resistance characteristic than that of TPU film.

3.5. Photooxidation Index and Synergistic Aging Effect. In order to express the aging extent of the films after exposure,

Figure 6 shows PI of TPU film exposed to O_3 , UV and O_3 /UV environment and of M-TPU film exposure to O_3 /UV environment, wherein “ $O_3 + UV$ ” represents the arithmetic sum obtained as a result of PI of TPU film after the same time of exposure to O_3 environment and to UV radiation in a separate case. As shown in Figure 6(a), PI of TPU film increases slightly with increasing exposure time after exposure to O_3 environment or to UV radiation in separate case, respectively, for example, the maximum PI of TPU film is 3.34 during 200 h of exposure to O_3 environment, 3.28 after 200 h of exposure to UV radiation, while the arithmetic sum of PI of TPU film after 200 h of exposure to O_3 environment and to UV radiation in separate case is 4.80. However, it increases remarkably with increasing exposure time after exposure to O_3 /UV environment; for example, the maximum PI of TPU film is 26.05, which is much bigger than 4.80 of the above arithmetic sum; namely, the curve of “UV/ O_3 ” is much higher than that of “ $O_3 + UV$ ” at the same time of exposure, which suggests that synergistic aging effect between ozone aging and UV-aging is more and more remarkable for TPU film during 200 h of exposure when PI is used as evaluation index. This can be attributed to the following reasons. UV light provided enough energy for TPU aging, and ozone may work as an oxidant for TPU degradation, which may accelerate the aging process of TPU. O_3 /UV aging changes physical and chemical characteristics of the films surface resulted in rapid color change and degradation, which may involve photo-oxidation of the aromatic functional groups and direct photolytic cleavage of the urethane group producing a diquinone imide [6].

As shown in Figure 6(b), it can be seen that PI of TPU and M-TPU films increases with increasing exposure time; furthermore, PI of M-TPU film is much lower than that of TPU film after the same time of exposure, which means the aging resistance characteristic of the composite UV absorber is distinct.

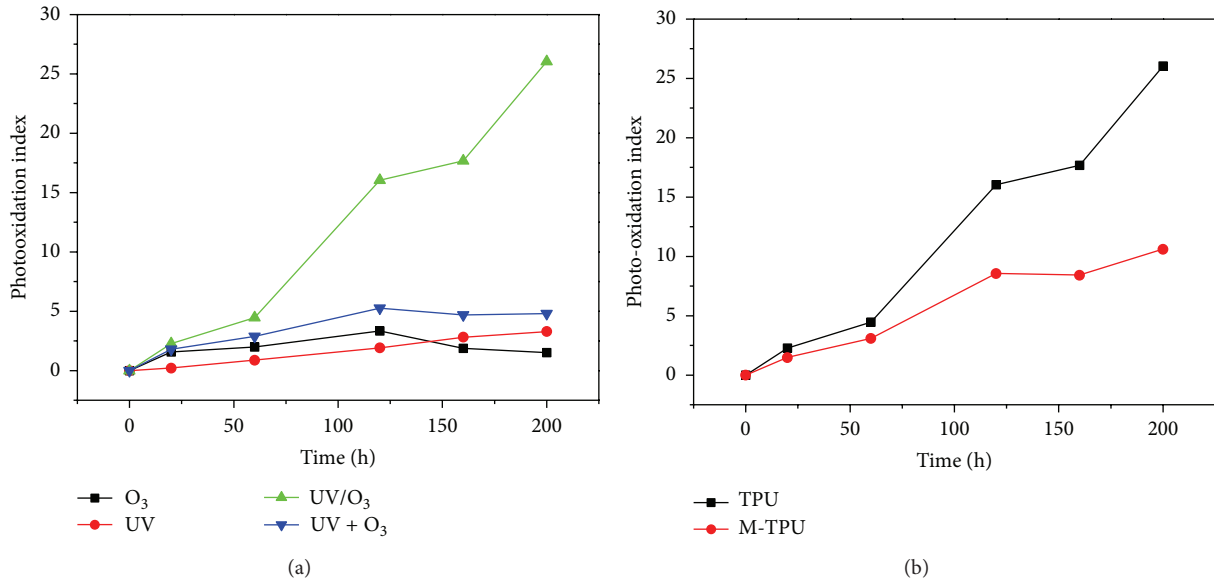


FIGURE 6: PI of TPU film exposed to different environments (a) and of TPU and M-TPU films exposure to O₃/UV environment (b).

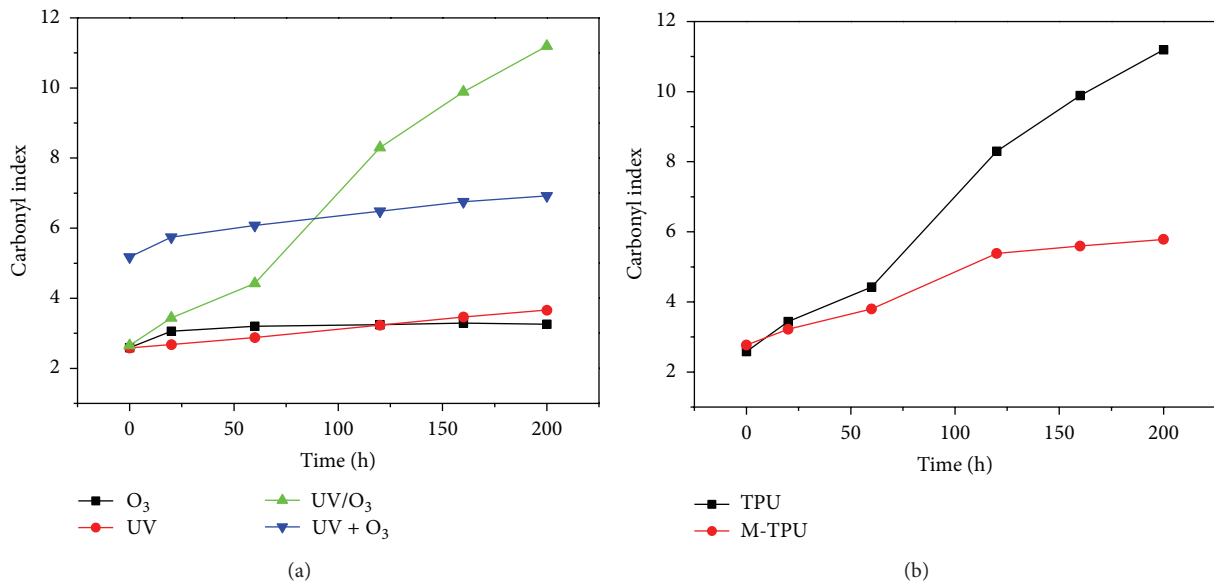


FIGURE 7: CI of TPU film exposed to different environments (a) and of TPU and M-TPU films exposure to O₃/UV environment (b).

3.6. Carbonyl Index and Synergistic Aging Effect. For a more quantitative expression of the aging extent, Figure 7 presents CI of TPU film exposed to O₃, UV, and O₃/UV environment and of M-TPU film exposure to O₃/UV environment, wherein “O₃ + UV” represents the arithmetic sum obtained as a result of CI of the films after the same time of exposure to O₃ environment and to UV radiation in separate case. As shown in Figure 7(a), CI of TPU film almost maintains 2.59~3.67 during 200 h of exposure to O₃ environment or to UV radiation in separate case, for example, CI of TPU film changes from 2.59 to 3.29 during 200 h of exposure to O₃ environment, and 2.59 to 3.67 after 200 h of exposure to UV radiation, while the arithmetic sum of CI of TPU film after 200 h of exposure to O₃ environment and to UV radiation in separate

case is 6.92. However, CI of TPU film almost increases linearly with incremental exposure time after exposure to O₃/UV environment; for example, the maximum CI of TPU film is 11.20, which is much bigger than 6.92 of the above arithmetic sum. The curve of “O₃/UV” is more and more higher than that of “O₃ + UV” after 100 h of exposure, which suggests that the synergistic aging effect exists in O₃/UV aging of TPU film after 100 h of exposure when CI is used as evaluation index. It is regretful that synergistic aging mechanism between ozone aging and UV aging has not been clarified till now.

As shown in Figure 7(b), CI of TPU and M-TPU films increases with increasing exposure time; however, CI of M-TPU film is much lower than that of TPU film after the same time

of exposure, which may be related to the protection effect of the composite UV absorber in M-TPU film. The composite UV absorber imparts better photo-oxidation resistance as they absorb UV light and reduce the rate of TPU degradation at the preliminary stage of aging. Unfortunately, we could not research the synergistic aging mechanism till now. More detailed work needs to be done.

4. Conclusion

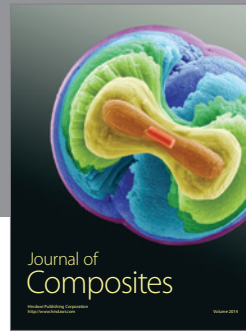
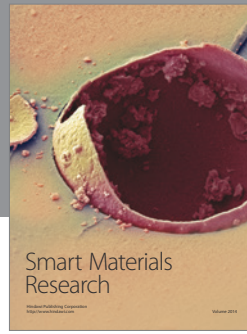
The composite UV absorber containing ZnO and CeO₂ nanoparticles and UV-531 and UV-327 has better protection for TPU system, which reduces distinctly the degradation of TPU film. Of course, the formula of the composite UV absorber needs further improvement for industrial application.

PI of TPU and M-TPU films increases with increasing exposure time. PI of M-TPU film is much lower than that of TPU film after the same time of exposure. Synergistic aging effect exists between ozone aging and UV aging when PI is used as evaluation index.

CI of TPU and M-TPU films increases with increasing exposure time. CI of M-TPU film is much lower than that of TPU film after the same time of exposure. The synergistic aging effect exists in O₃/UV aging of TPU film after 100 h of exposure when CI is used as an evaluation index.

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