

UV Photodegradation of Polypropylene Thick Bars Containing Rutile-type TiO₂ Nanorods^{*}

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Abstract Surface modified rutile-type titanium dioxide (CST) nanorods were used as a UV absorber in polypropylene (PP) thick bars in combination with the hindered amine light stabilizer (HALS) Chimassorb[®] 944 (C944). For all of the tested samples, the photodegradation was mainly limited in the region near the exposed surface, as proved by the carbonyl index and molecular weight. Compared with the typical HALS photostabilization system containing organic hindered phenol UV absorber Tinuvin[®] 328 (T328), the thickness of photodegradation region for PP/C944/CST was only a quarter to that for PP/C944 and PP/C944/T328, while the rates of reduction in molecular weight and increase in carbonyl index were much lower. Optical microscopic observation showed that the evolution of surface micro-cracks in PP/C944/CST was quite different from that in the other samples, while scanning electronic micrographs revealed that the depth of the micro-cracks in PP/C944/CST was much shorter than that in the others. It is therefore concluded that the protection of CST on PP thick bars is mainly attributed to the outstanding UV-shielding and cracks-blocking abilities.

Keywords: Polypropylene; Titanium dioxide nanorods; Photodegradation; Molecular weight; Surface micro-cracks.

INTRODUCTION

Polypropylene (PP) is one of the most widely used polymers because of its attractive combination of processability, mechanical properties and chemical resistance^[1]. However, the poor stability of PP against ultraviolet (UV) radiation limits its versatile application to some extent^[2], especially for the products used outdoors. Compounding with UV absorbers and stabilizers is an effective and commercial way to protect PP materials from harmful UV irradiation and extend their service life^[3–5]. Traditional organic UV absorbers are effective but will lose efficiency due to their leaching, migration and consumption during the usage^[5, 6]. For this reason, recent research works are focused on novel inorganic UV absorbers, especially, nanometric metal oxides, such as titanium dioxide (TiO₂) and zinc oxide nanoparticles^[7–10]. With the objective to identify their mechanism, a number of studies have been conducted on the photodegradation behavior of inorganic nanoparticles and/or organic UV absorber stabilized polymer blends^[3, 5, 10, 11].

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In addition to sheets (films) and fibers, PP can also be made into profiles of various thicknesses and widely used in civilian products, automotive and construction industries. The photodegradation of polymer sheets and fibers may be simply considered homogeneous because they are thin in one or two dimensions. On the contrast, the photodegradation of thick samples is much complicated and usually inhomogeneous, because the intensity of UV radiation and concentration of oxygen differ very much in regions of different depth from the exposed surface^[12–19]. The inhomogeneous degradation usually leads to the formation of a degraded surface region and surface micro-cracks which can cause a severe loss of fracture resistance^[14, 16, 20–23] that makes life time estimation of PP thick products a complex issue. For this reason, it is necessary to pay attention to their weathering studies.

The UV degradation profile of PP thick bars is associated with the photostabilization system. For unstabilized PP thick bars, Schoolenberg and Vink^[14] obtained a ‘shoulder’-like carbonyl concentration profile consisting of a plateau region at the exposed surface and a sharp decrease at some distance from the surface. The ‘shoulder’ shifted to deeper regions in the course of time due to the oxygen diffusion by surface micro-cracks. For PP stabilized by hindered amine light stabilizer (HALS) system containing 0.3% Tinuvin[®] 770, 0.3% Chimassorb[®] 944 and 0.3% Irganox[®] B215, White and colleagues^[16, 17] reported little variation in molecular mass through the depth for any chosen exposure time. In the interior the fall in average molecular mass was even greater than that observed in unstabilized PP. They speculated that the observation was a consequence of decreased oxygen consuming at surface and the residual stresses in the moldings. As UV absorbers, Tinuvin[®] 326 produced relatively small differences in the shape and depth of the degradation profile while a pigment grade TiO₂ caused the decline of molecular mass to fall to a minor level^[14, 16].

In comparison with the micrometric powders, the nanometric particles have broader prospects considering their superior UV light screening effects and lower influence to the color and transparency of polymers when well dispersed^[24]. Their possible influence on the crystallization and oxygen barrier properties of polymers made the mechanism of photostabilization more complex^[21, 25].

In our previous research^[26], the calcined silica-coated rutile-type TiO₂ (CST) nanorods have been prepared and used as UV absorber for PP films. It has been proved that, when compounded with HALS Chimassorb[®] 944, the CST nanorods demonstrated excellent efficiency in the photostabilization efficiency of PP. In this work, the UV degradation behavior of thick bars of PP nanocomposites was characterized by determining the evolution of micro-cracks, carbonyl index and molecular weight in regions of different depths from the exposed surface. The UV-stabilization mechanism of CST was presented.

EXPERIMENTAL

Materials and Sample Preparation

The preparation of the calcined silica-coated rutile-type TiO₂ nanorods (CST), with a TiO₂/SiO₂ ratio of 1:1, has been reported in our previous paper^[26]. Additive-free polypropylene (PPH-XN-N45), with an MFI of 4.8 g per 10 min (230 °C and 2.16 kg load), was supplied in powder form by China National Petroleum Corporation. The HALS, Chimassorb[®] 944, and the hindered phenol UV absorber, Tinuvin[®] 328, were obtained from Ciba Specialty Chemicals (China) and are denoted as C944 and T328 hereafter, respectively.

The PP compositions were prepared using a TSE-30 corotating twin-screw extruder (Diameter Φ = 30 mm, length/diameter L/Φ = 40, Nanjing Ruiya Polymer Processing Equipment Ltd., China). The operation temperature was maintained at 175, 185, 190, 200, 200, 200, 200, 200 and 200 °C from hopper to die of the extruder, while the screw speed was set up to 200 r/min. After cooling in water, the extrudates were pelletized. Pelletized blend samples from the mixing experiments were injection molded into specimens with dimension of 80 mm × 10 mm × 4 mm, using a UA120A injection molding machine (Guangdong Yizumi Precision Machinery Co., Ltd., China).

The contents of CST, C944 and T328 were all fixed at 0.3 wt% in different for each compositions. The antioxidants Irganox[®] 1010 and Irgafos[®] 168 were used as processing stabilizers and added to each formulations at 0.2 wt% and 0.1 wt%, respectively.

Exposure Conditions

The photodegradation of the various PP compositions was carried out upon UVB irradiations at 40 °C in air in a CL-1000 Ultraviolet Crosslinker (UVP LLC, USA) for different periods in the range of 0–500 h. The composition samples were placed 12 cm away from the light source with an exposure of 80000 $\mu\text{J}/\text{cm}^2$. The UVB light, emitted from G8T5E lamps (Ushio, Japan) with peak emission at 302 nm, was chosen as the radiation source for the photodegradation because it could result adequate degradation rate of PP for getting clear results in limited time periods.

Characterizations

The dispersion of nanoparticles in PP matrix was observed by using a 2200FS high resolution transmission electron microscope (TEM, JEOL Ltd., Japan) operating at an accelerating voltage of 200 kV.

The UV transmission characteristics of the unexposed samples in the chosen wavelength range (295–320 nm) were determined by measuring the intensity transmitted through bars placed between the UV source and the spectrometer detector with a UV-2600 UV-Vis spectrophotometer (Shimadzu Corporation, Japan). Samples with different thicknesses were prepared by slicing the 80 mm $\times$ 10 mm $\times$ 4 mm bars at given depths and the machined surface was polished before testing.

Differential scanning calorimetry (DSC) characterization was performed on a Q2000 instrument (TA Instruments) to investigate the crystallization behavior. The heating and cooling rates used were the same as 10 K/min. The crystallinity for the samples was calculated according to the DSC data. The enthalpy of melting for 100% crystalline PP was taken to be $\Delta H_m^0 = 209 \text{ J/g}$ ^[27].

The O₂ permeability coefficients of the PP compositions were measured based on ASTM D 1434 by a VAC-V2 Oxygen Permeation Tester (Labthink Instruments Co., Ltd., China) at 23 ± 2 °C. Diffusion coefficient was obtained by the time lag of permeation and the solubility was calculated using solution-diffusion model^[28].

Surface cracking for samples exposed to the UV irradiation was observed using a BX51 optical microscope (OM, Olympus Ltd., Japan) and an S-4300F scanning electron microscope (SEM, JEOL Ltd., Japan). Sample observation was taken every 10 h in the initial 100 h UV exposure and every 100 h thereafter. The depth profile of micro-cracks was measured by observing the longitudinal section, which was cut along the direction perpendicular to the micro-crack. The scanning rate of SEM was 0.5 mm/s.

For determining the depth profile of the photodegradation, the exposed bars were sliced at different depths from the exposed surface using a RM2155 rotary microtome (Leica Microsystems Inc., Germany) at a cutting pass of 0.05 mm. The material removed was collected for measuring the molecular weight and the new bar surface was subjected to determination of carbonyl groups.

The molecular weight was measured by gel permeation chromatography (GPC). The samples were extracted from the surface (0–0.2 mm), subsurface (0.2–0.3 mm), center (1.9–2.1 mm) and bottom (3.8–4.0 mm) regions of each bar. The data obtained for each depth are represented by the mid-point of the region, *i.e.* the data for first region were plotted at 0.1 mm and the data for the second region are plotted at 0.3 mm, *etc.* The GPC experiments were carried out using a PL-GPC 220 high temperature GPC/SEC System (Agilent Technologies, United States) at 150 °C coupled with a RI detector. The column set consists of two columns PL Mixed-B-LS (Polymer Laboratories). The eluent was 1,2,4-trichlorobenzene (Merck Co., Ltd., Germany) stabilized with diphenylamine (Merck Co., Ltd., Germany). Aggregate-free polypropylene solutions were prepared by controlling storage times at 150 °C in mixtures with stabilizers. A PL-SP 260VS sample preparation system (Agilent Technologies, United States) was used for the dissolution and filtration of samples prior to GPC analysis.

The carbonyl contents of longitudinal cutting slices of exposed bars were obtained at attenuated total reflectance (ATR) mode using a Nicolet iN10 Fourier transform infrared (FTIR) microscope (Thermo Fisher Scientific Inc., USA) in the wavenumber range of 4000–650 cm^{-1} and were signal averaged over 16 scans at a resolution of 4 cm^{-1} . Carbonyl groups were easily detected in the broad infrared region at 1800–1680 cm^{-1} for oxidized PP. In order to minimize deviations from sample thickness, the peak at 2722 cm^{-1} , which is associated

with CH bending and CH₃ stretching^[29], was used as an internal reference. The carbonyl growth was expressed by carbonyl index (CI):

$$CI = \frac{A_{C=O}}{A_{2722}}$$

where $A_{C=O}$ and A_{2722} were the absorbance of carbonyl and the internal reference, respectively.

RESULTS AND DISCUSSION

Influence of TiO₂ Nanoparticles on Surface Micro-cracks of PP Thick Bars under UV Irradiation

The photodegradation of a polymer bar starts on the exposed surface accompanying by the formation of micro-cracks on the surface upon the UV exposure. The degraded and embrittled surface will lead to the loss in fracture properties. In order to study the formation and propagation of surface micro-cracks, optical microscopic observation was performed on the thick PP bars during UV exposure. The micrographs were taken on the center part of PP specimens at different exposure periods. Figure 1 shows the evolution of surface micro-cracks at different UV exposure time.

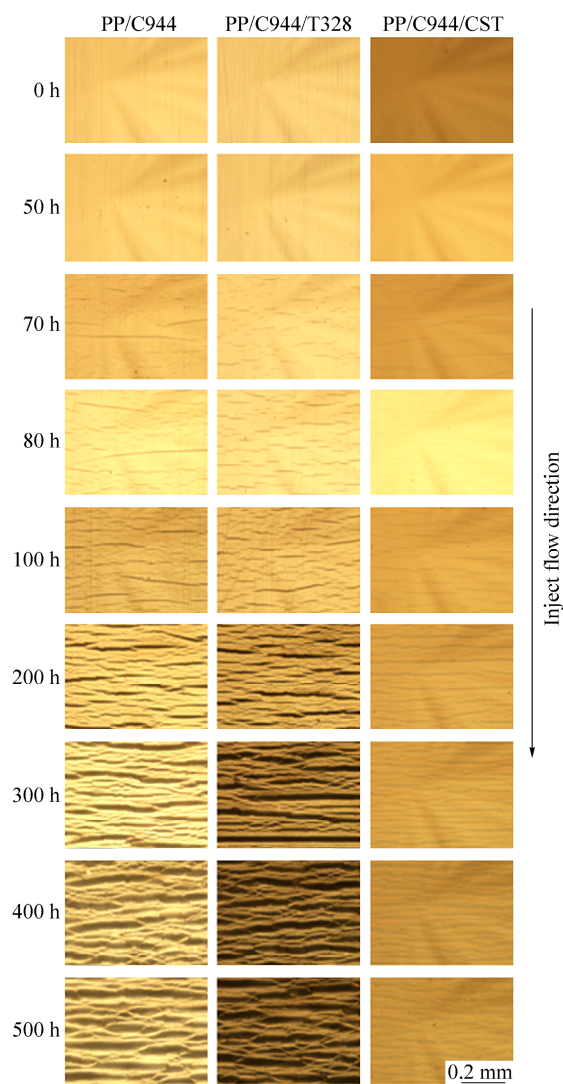


Fig. 1 Optical micrographs showing evolution of surface micro-cracks during UV exposure

As shown in Fig. 1, the parallel pattern grows spontaneously during exposure. In the beginning, there were only several scratch traces caused by injection molder but no micro-cracks on the surface of non-degraded samples. The spontaneous micro-cracks, perpendicular to the flow direction of the injection-molding, appeared after 50–70 h UV exposure and could be seen over the surface. By increasing irradiation duration, the length and width of the micro-cracks all increased while lots of small new micro-cracks formed. After 200 h UV exposure, the micro-cracks further propagated and intersected. Gradually, a coarse mesh-like surface formed after 400 h exposure (PP/C944 and PP/C944/T328). From 400 h to 500 h, the changes of surface micro-cracks were not obvious, because the surface degradation was serious enough to achieve a limit state. Obviously, the surface micro-cracks of PP/C944/CST were narrower and smaller than those of the others at every moment. Even after 500 h exposure, they were almost discrete and much finer than the others. The severe micro-cracks in the surface, as documented by OM, indicated that degradation was not limited to the surface but may take place even at larger depths.

SEM micrographs can show more details of the surface micro-cracks, especially their depth. As shown in Fig. 2, although the cutting (perpendicular to the micro-crack direction) made several rifts to gaps, the depth profile of micro-cracks could be measured by observing the longitudinal section. These micro-cracks formed and propagated toward the interior of the specimens during UV exposure. Therefore, the micro-cracks formed earlier were deeper than the later formed ones. These micro-cracks with different depth formed a brittle region distinguished from the deeper ductile region. In particular, after 500 h exposure, the surface region was seriously broken. These results showed that the degradation caused by UV irradiation was most serious in the surface region of polymer materials.

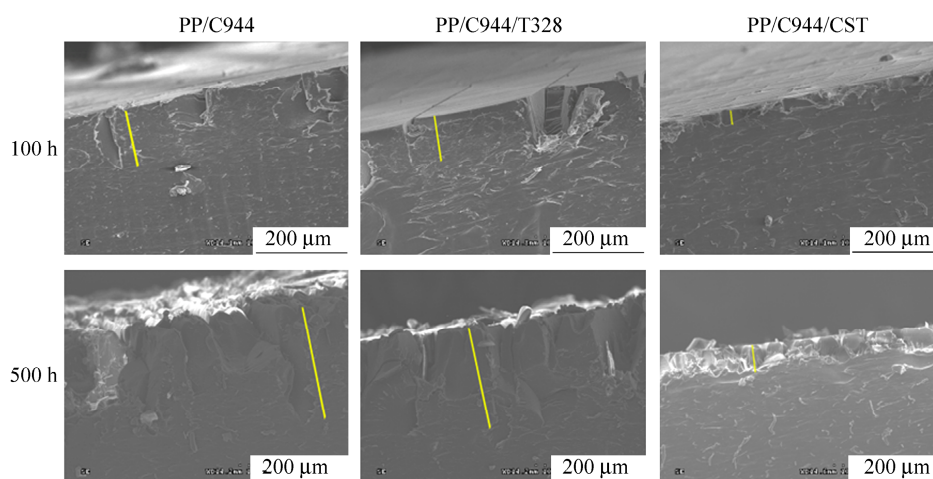


Fig. 2 Surface micro-cracks after 100 h and 500 h UV exposure (The line segments point out the largest depth of the micro-cracks in the samples.)

The thickness of surface micro-crack region, which is defined as the maximum depth of micro-cracks, was measured by statistics from multiple SEM images. As shown in Fig. 3, the thickness of surface micro-crack region increased with exposure time. The growth rate was rapid in the early stage and slowed down later. From 100 h to 500 h exposure, the thickness of surface micro-crack region increased from 0.110 mm to 0.240 mm for PP/C944 and from 0.100 mm to 0.210 mm for PP/C944/T328. It indicates that the presence of T328 produced relatively little differences in the micro-crack depth upon UV exposure. On the other hand, the micro-crack morphology of these two samples was very similar, as shown in the OM micrographs (Fig. 1). When the CST nanorods were introduced into the PP compositions instead of T328, the growth rate of the micro-crack depth reduced dramatically and the thickness of surface micro-crack region reached to only 0.025 mm, corresponding to about a quarter of that for PP/C944 and PP/C944/T328. As the sample was exposed for 500 h, the thickness

increased doubled to 0.055 mm but always keeping the same reduction level. This result indicated that the presence of CST can prevent the micro-crack propagation effectively.

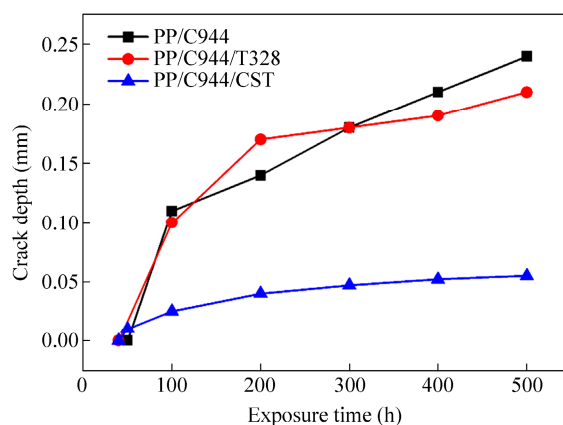
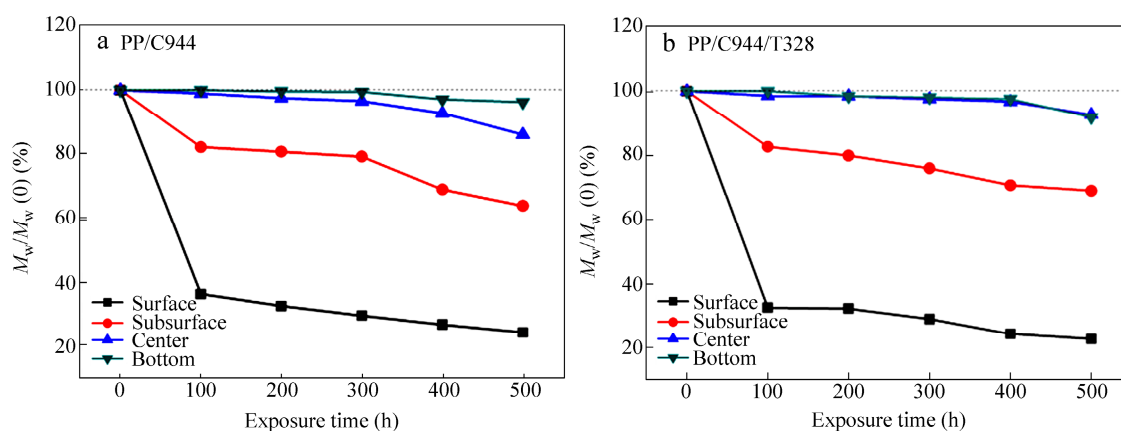


Fig. 3 Crack depth of PP thick bars versus UV exposure time

Influence of TiO₂ Nanoparticles on Molecular Weight

As discussed previously, during 0–500 h exposure time, the spontaneous micro-cracks appeared predominantly located in the region near surface of the thick bars. In order to explore the difference between top surface and beneath PP matrix, the molecular sizes of PP in surface (0–0.20 mm), subsurface (0.20–0.40 mm), center (1.90–2.10 mm) and bottom (3.80–4.00 mm) regions were measured by GPC analysis. The weight-average molecular weight (M_w) in each region of samples was used to follow the progress of degradation. For better comparison, the ratio of molecular weight to the initial molecular weight ($M_w/M_w(0)$) was measured with exposure time (Fig. 4).

As show in Fig. 4(a), without any UV absorber, the PP/C944 was corroded and degraded gradually with the depth, which is very different from the results in Ref.15, where another HALS (Tinuvin[®] 770) was present in the tested sample. The value of M_w in the surface region was very low for all exposure times. It decreased most seriously during the first 100 h (dropped by 60% off) and declined 10% linearly during 100–500 h. The M_w of subsurface region fell 20% off in 0–100 h and declined another 20% in 100–500 h. There was gentle but evidently detectable degradation in the center and bottom regions since 200 h and 400 h respectively. For PP/C944/T328 that contained the UV absorber Tinuvin[®] 328, as shown in Fig. 4(b), the degradation trends of surface and sub-surface regions were almost the same as those for PP/C944. The difference was that a synchronized decline in the center and bottom regions was observed after 400 h exposure. Figure 4(c) shows that



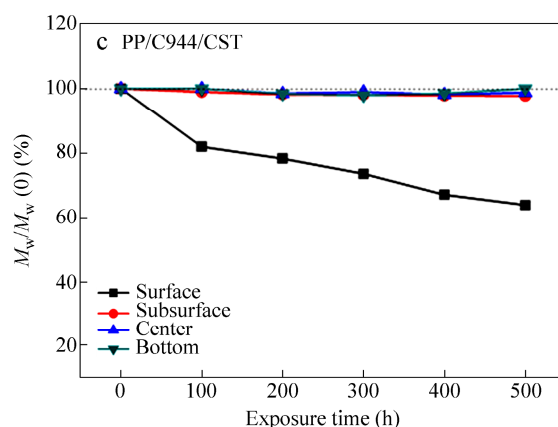


Fig. 4 $M_w/M_w(0)$ of specimens in different regions of PP thick bars versus UV exposure time

the behavior of PP/C944/CST was quite different from that of PP/C944 and PP/C944/T328. The photodegradation occurred only in the surface region with a slow rate and M_w retained 65% of its original value after 500 h, meanwhile in the other regions, the molecular weight kept almost invariant. That means the addition of CST nanorods constrained the degradation of PP in the top surface region and protected the beneath matrix from harmful UV radiation effectively.

Influence of UV Absorber on Carbonyl Concentration

The depth profiles of carbonyl index (CI) after 100 h exposure are presented in Fig. 5. The CI reduced dramatically with the exposure depth, suggesting that the oxidative photodegradation took place in the region near the exposed surface. It is seen that the dramatic reduction of CI occurred in the surface micro-crack regions, where the depths were 0.100, 0.110 and 0.025 mm for PP/C944, PP/C944/T328 and PP/C944/CST, respectively. Below the surface micro-crack regions, the photodegradation proceeded moderately along the exposure depth and finally the values of CI reached to the background level, under which chemical changes did not occur actually. It is observed that the depth of the entire regions of the photodegradation were about three times large of the surface micro-crack regions, *i.e.*, ~ 0.3 mm for PP/C944 and PP/C944/T328 and ~ 0.07 mm for PP/C944/CST. By comparison with the depth profiles of carbonyl index of the tested samples, it is indicated that, as an inorganic UV absorber, the CST nanorods are effective to restrict the photodegradation of PP at a low rate and in a thinner region with respect to the organic counterpart T328.

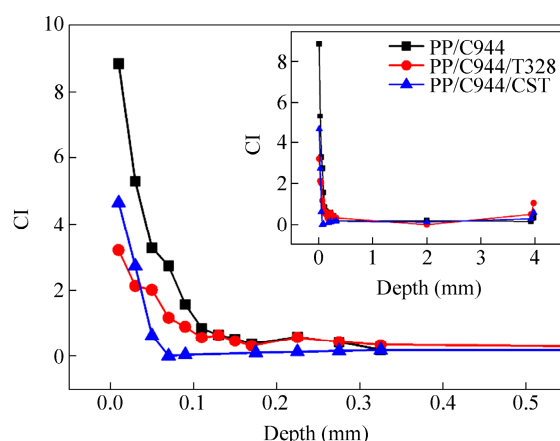


Fig. 5 Depth profile of carbonyl index after 100 h UV exposure

Discussion on Mechanisms

The photodegradation of PP thick bars was affected by many factors. As a kind of semicrystalline polymer, the crystallinity of PP is important, because the non-crystalline region is easier to degrade than the crystalline region. The O₂ permeability and UV shielding ability of the samples also affect the inner environment for photo-oxidation. In order to identify the difference of mechanism between CST/HALS and T328/HALS stabilization systems, further experiments were performed on the un-exposed samples.

Crystallinity of PP in the compositions

Thermal and crystallization data for PP samples before UV exposure are summarized in Table 1. The addition of T328 and CST all benefited to improve the melting behavior of PP/C944. Although the crystallization temperature remained the same or even shifted to lower value, the crystallinity (X_c) increases slightly by incorporation of T328 and CST, from 36.5% for PP/C944 to 39.4% for PP/C944/T328 and 37.6% for PP/C944/CST. It seems that the crystallinity is not correlated to the molecular weight or the carbonyl index for samples tested in the present work.

Table 1. Thermal and crystallization data for PP compositions before UV treatment

Sample	H_f (J/g)	T_m (°C)	H_c (J/g)	T_c (°C)	X_c (%)
PP/C944	85.1	162.6	91.7	120.2	36.5
PP/C944/T328	94.6	163.4	99.3	120.2	39.4
PP/C944/CST	87.2	162.3	91.6	119.5	37.6

Oxygen permeability

The O₂ permeability of a polymer is an important factor for its oxidative degradation. Previous research established that the degradation profile of thick polyolefin samples is corresponding to the oxygen diffusion or the rate of oxygen supply^[12, 13]. Nanofillers, such as organoclay that can inhibit the oxidation of polymer, partly because their contribution to the O₂ barrier property^[30]. In order to explore this issue, the O₂ permeability coefficients in the PP compositions were measured, as shown in Table 2. It is seen that either CST or T328 affects little on the O₂ barrier property in the PP films. For PP/C944/CST, the O₂ permeability showed some reduction but still maintained about 90% of that of the PP/C944. That might be due to their little content. In short, it is believed that the change of barrier property does not play important role on the photodegradation.

Table 2. The permeation test results

Sample	Permeability coefficient (cm ³ ·[STP]·cm/cm ² ·s·cmHg)	Diffusion coefficient (cm ² /s)	Solubility (cm ³ ·[STP]/cm ³ ·cmHg)
PP/C944	1.027×10^{-10}	1.134×10^{-7}	9.043×10^{-4}
PP/C944/T328	1.034×10^{-10}	3.540×10^{-7}	9.972×10^{-4}
PP/C944/CST	9.131×10^{-11}	1.231×10^{-7}	7.816×10^{-4}

Dispersion of CST nanorods and UV transmission

In our previous research^[26], it has been established that the CST nanorods had high efficiency of protecting PP films from harmful UV radiation because of the good dispersion and UV shielding ability. In this work, the morphology of the PP/C944/CST nanocomposite was further observed by TEM. As can be seen from the TEM images (Fig. 6), most of CST nanorods were well dispersed in PP matrix meanwhile the geometry of CST was maintained.

The relative intensity of UV radiation transmitted through given thicknesses (0.05, 1 and 2 mm) of the PP compositions is used as the simulation of UV radiation at the depth from the exposed surface of the degrading polymer bars. As shown in Fig. 7, the UV transmission through the bars containing UV absorbers (T328 and CST) was very much lower than that through the absorber-free bars. PP/C944/CST transmits less than the PP/C944/T328 obviously. That means the well-dispersed CST nanorods are a kind of effective UV shielding agent for PP thick bars. In fact, the UV transmission through the 2 mm specimen of PP/C944/CST was too weak to be detected.

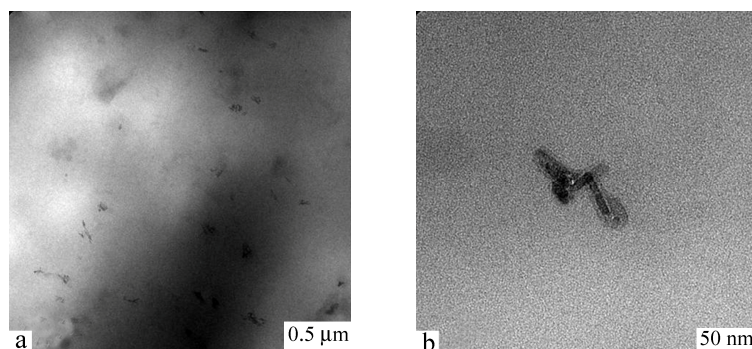


Fig. 6 TEM images for PP/C944/CST

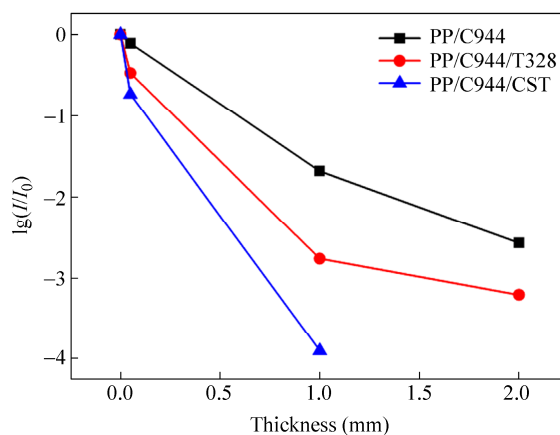


Fig. 7 UV transmittance versus sample thickness

In summary, the presence of CST and T328 as UV absorbers can effectively diminish the UV intensity through the PP thick bars, while the changes in crystallinity and O₂ barrier property play less important role.

As described above, the UV exposure caused decrease in molecular weight and increase in carbonyl concentration of the PP matrix, accompanied by the formation of micro-cracks in the near-surface region of the tested specimens. Although T328 can block the UV transmission to some extent (Fig. 7) and decrease the CI value in the degraded region, it produced negligible effects on the behavior of micro-cracks and M_w . It is because the wedge-shape micro-cracks produced earlier will provide pathways for UV radiation and oxygen and result in the photo-oxidation of the PP matrix nearby. However, as a kind of nanometric UV absorber which may have toughening and reinforcing effects on polymers^[31, 32], the CST nanorods could constrain the photo-oxidation in a thinner region because they inhibited the propagation of micro-cracks along the direction of UV radiation.

CONCLUSIONS

Results obtained in the present research indicate that the presence of CST nanorods in the PP matrix can help to reduce the extent of photo-oxidation and constrain the degradation (micro-cracks formation and M_w reduction) in a thinner surface region with respect to the organic UV absorber T328. Owing to its low content, the CST has little contribution to crystallinity and O₂ barrier properties of un-exposed PP matrix. The anti-aging mechanism of CST mainly thanks to its outstanding UV-shielding ability when it is well dispersed. Moreover, the early-stage restriction on the micro-crack growth also benefits to prevent the formation of UV and O₂ channel and protect the beneath polymer matrix.

By comparison between the PP/C944/CST and PP/C944/T328 systems, the synergistic effect of the CST nanorods was stronger than the organic UV absorber T328. Although the existence of T328 improved the UV shielding property and inhibited the carbonyl production, it had no obvious effects on maintaining the surface

property and molecular weight of thick PP bars. That means a single method for photodegradation description may lead to a biased result.

The present work demonstrated the great potential of the rutile-type TiO₂ nanorods in the photostabilization of polymers. As inorganic nanoparticles, the CST nanorods are more stable than the conventional organic UV absorbers and resistant to migration. Because of their great effect on UV-shielding and photostabilization not only for PP thin films but also thick bars, it is expected the CST nanorods could find practical applications in the protection of polymers against photodegradation. Intensive research is under progress and will be reported in the future.

REFERENCES

- 1 Tripathi, D., "Practical Guide to Polypropylene", by Rapra Technology Limited, UK, 2002, p. 2
- 2 Ojeda, T., Freitas, A., Birck, K., Dalmolin, E., Jacques, R., Bento, F. and Camargo, F., *Polym. Degrad. Stab.*, 2011, 96: 703
- 3 Basfar, A.A., Ali, K.M.I., Vaidya, M.M., Bahamdan, A.A. and Alam, M.A., *Polym-Plast. Technol.*, 2010, 49: 841
- 4 White, J.R. and Turnbull, A., *J. Mater. Sci.*, 1994, 29: 584
- 5 Pospíšil, J. and Nešpurek, S., *Prog. Polym. Sci.*, 2000, 25: 1261
- 6 Parejo, P.G., Zayat, M. and Levy, D., *J. Mater. Chem.*, 2006, 16: 2165
- 7 Kumar, A.P., Depan, D., Singh Tomer, N. and Singh, R.P., *Prog. Polym. Sci.*, 2009, 34: 479
- 8 Wen, B., Wang, F., Xu, X.F., Ding, Y.F., Zhang, S.M. and Yang, M.S., *Polym-Plast. Technol.*, 2011, 50: 1375
- 9 Li, Y., Yang, Y. and Fu, S., *Compos. Sci. Technol.*, 2007, 67: 3465
- 10 Aloui, F., Ahajji, A., Irmouli, Y., George, B., Charrier, B. and Merlin, A., *Appl. Surf. Sci.*, 2007, 253: 3737
- 11 Allen, N.S., Edge, M., Ortega, A., Sandoval, G., Liauw, C.M., Verran, J., Stratton, J. and McIntyre, R.B., *Polym. Degrad. Stab.*, 2004, 85: 927
- 12 Furneaux, G.C., Ledbury, K.J. and Davis, A., *Polym. Degrad. Stab.*, 1981, 3: 431
- 13 Cunliffe, A.V. and Davis, A., *Polym. Degrad. Stab.*, 1982, 4: 17
- 14 Schoolenberg, G.E. and Vink, P., *Polymer*, 1991, 32: 432
- 15 Tavares, A.C., Gulmine, J.V., Lepienski, C.M. and Akcelrud, L., *Polym. Degrad. Stab.*, 2003, 81: 367
- 16 Turton, T.J. and White, J.R., *Polym. Degrad. Stab.*, 2001, 74: 559
- 17 White, J.R. and Shyichuk, A.V., *Polym. Degrad. Stab.*, 2007, 92: 2095
- 18 Cao, H., Yuan, J.P., Zhang, R., Huang, C.M., He, Y., Sandreczki, T.C., Jean, Y.C., Nielsen, B., Suzuki, R. and Ohdaira, T., *Macromolecules*, 1999, 32: 5925
- 19 Zhang, R., Chen, H., Cao, H., Huang, C.M., Mallon, P.E., Li, Y., He, Y., Sandreczki, T.C., Jean, Y.C., Suzuki, R. and Ohdaira, T., *J. Polym. Sci. Part B: Polym. Phys.*, 2001, 39: 2035
- 20 Schoolenberg, G.E., *J. Mater. Sci.*, 1988, 23: 1580
- 21 Zhao, H. and Li, R.K.Y., *Polymer*, 2006, 47: 3207
- 22 Geburtig, A. and Wachtendorf, V., *Polym. Degrad. Stab.*, 2010, 95: 2118
- 23 Schoolenberg, G.E. and Meijer, H.D.F., *Polymer*, 1991, 32: 438
- 24 Calvo, M.E., Castro Smirnov, J.R. and Míguez, H., *J. Polym. Sci. Part B: Polym. Phys.*, 2012, 50: 945
- 25 Paul, D.R. and Robeson, L.M., *Polymer* 2008, 49: 3187
- 26 Qi, L., Ding, Y.F., Dong, Q.X., Wen, B., Wang, F., Zhang, S.M. and Yang, M.S., *J. Appl. Polym. Sci.*, DOI: 10.1002/app.40601
- 27 Brandrup, J. and Immergut, E.H., "Polymer handbook, Part V, 3rd, ed.", Wiley, New York, 1989, p. 27
- 28 Cornelius, C.J., "Physical and gas permeation properties of a series of novel hybrid inorganic-organic composites based on a synthesized fluorinated polyimide." PhD Thesis, Virginia Polytechnic Institute and State University, USA, 2000
- 29 Rabello, M.S. and White, J.R. *Polym. Degrad. Stab.*, 1997, 56: 55
- 30 Mirzadeh, A. and Kokabi, M., *Eur. Polym. J.*, 2007, 43: 3757
- 31 Asmatulu, R., Mahmud, G.A., Hille, C. and Misak, H.E., *Prog. Org. Coat.*, 2011, 72: 553
- 32 Pan, Y., Xu, Y., An, L., Lu, H., Yang, Y., Chen, W. and Nutt, S., *Macromolecules*, 2008, 41: 9245