

Effects of Coupling Agents on the Natural Aging Behavior and Oxidation Profile of High-Density Polyethylene/Sericite Composites

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ABSTRACT: The natural photooxidation of high-density polyethylene (HDPE)/sericite composites was carried out outdoors for 180 days. The oxidative products, oxidation profile, and section morphology were characterized with Fourier transform infrared spectroscopy, infrared microscopy, and scanning electron microscopy, respectively. The results showed that HDPE/sericite had a higher oxidation degree than HDPE. All the coupling agents (CAs) accelerated the oxidation reaction of HDPE and made the final carbonyl index higher than that of an untreated one. The effect of sericite might have been due to the increased ultraviolet absorbance, whereas the effects of CAs might have been due to the active functional groups. Furthermore, cracks in the sections of test bars of HDPE/sericite

composites after natural exposure were also observed. Their average lengths and densities were different for various CA treatments. This difference had a direct correspondence with the oxidation profile along the depth. This demonstrated that significant oxidation and consequently chain scission in the surface layer were responsible for the formation of cracks. Comparing the natural aging behavior of the films with test bars, we obtained more information about the propagation of the photooxidation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 610–617, 2008

Key words: aging; composites; degradation; polyethylene (PE)

INTRODUCTION

Durability under practical conditions is of great importance for polymer materials. In long-term outdoor applications, polymer materials will suffer from the impact of environmental factors such as ultraviolet (UV) light, oxygen, temperature changes, and moisture. As a result, the mechanical properties deteriorate gradually, and this is accompanied by yellowing, a declining molecular weight, and fractures. The degradation of polymer materials causes tremendous loss in industry and daily life. Therefore, aging and anti-aging research of polymer materials is attracting more and more attention.

However, many material researchers are more interested in the mechanical properties of polymer materials than in their durability. In the past decades, polymer composites have become a focus of research. For example, lamellar fillers, such as mica and clay, exhibit an excellent ability to improve the flexural modulus, heat deflection temperature, warp-ge, and gas barrier performance and to cut down

the cost as well.^{1–5} However, so far the effects of inorganic fillers on the aging behavior of polymer materials have not been discussed thoroughly. Shen and coworkers^{6–8} reported that a sericite with a very high aspect ratio could provide perfect anti-UV ability in polypropylene (PP), natural rubber, phenol resins, and epoxy resins. They attributed this effect to the UV-shielding ability of sericite. Yang et al.,⁹ however, found that sericite accelerated the photooxidation of high-density polyethylene (HDPE). Qin and coworkers^{10–12} demonstrated that layered silicates have a negative effect on the stability of PP because of the active sites on the silicate layers, and the interlayer cations have a great influence. These experimental results show that various fillers have different influences on the natural stability of polymer materials, and some additives, such as intercalating agents, also possibly have an impact. However, inadequate research on the effects of coupling agents (CAs) has been reported. Further studies on the aging behavior and mechanism of polymer composites and the effects of inorganic fillers and surface treatments are quite important and instructive for material design to obtain materials with good mechanical properties and long durability as well.

In degradation research of polymer materials, films with thicknesses of 20–200 μm are often used. However, in outdoor applications, films, especially

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thick products such as plates, pipes, and rods, suffer from the impact of environmental factors, and the damage is often correlated with crack initiation and propagation in the matrix. How can we characterize the changes occurring in thick materials? How do the chemical structure and morphology evolve from the surface to the interior? Nagai et al.¹³ used an attenuated total reflectance technique to study a depth profile of polycarbonate after photochemical degradation. The results showed that the degradation rate was extreme in the region of 0–0.2 μm . White et al.¹⁴ studied the molecular weight and molecular weight distribution of 3-mm-thick test bars of polyethylene, PP, and epoxy resin (EP) along the depth with the aid of computer analysis. They found that macromolecular scissions and crosslinks in the cross sections had uneven distributions. A more powerful technique is infrared microscopy (IM) coupled with a microtome.^{15–19} For example, Gardette and coworkers^{15,16} studied the depth profiles of photodegraded polycarbonate, epoxy resins, and paint with this method.

In this study, the natural aging behavior and oxidation profile along the depth of HDPE/sericite composites were investigated. The effects of CAs were studied as well. The cross section was scanned by IM from the surface to the interior so that the oxidative evolution along the depth was obtained. Along with scanning electron microscopy (SEM), the section morphology and its relation to oxidation development were revealed. On the basis of the results, the aging mechanism of the HDPE/sericite composite was also discussed.

EXPERIMENTAL

Materials

HDPE (2100J; melt index (MI) = 6.5 g/10 min, density = 0.957 kg/m³) was acquired from Yanshan Petroleum Chemical Co. (Beijing, China); sericite with a high aspect ratio (800 mesh) was obtained from the Xichang Institute of Mineral Substances of Sichuan (Sichuan, China), and its basic components and properties are listed in Table I.⁶ Maleic anhydride (MAH) and acrylic acid (AA) were from Beijing Chemical Plant (Beijing, China); titanate $\{(\text{CH}_3)_2\text{CHOTi}[\text{OC}(\text{O})(\text{CH}_2)_{14}\text{CH}(\text{CH}_3)_2]_3\}$; NDZ-101, aluminate ($\text{C}_3\text{H}_7\text{OAlOCOROCORCOOR}$), and silane [$\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OC}_2\text{H}_5)_3$; KH550] were from Nanjing Shuguang Chemical Group Co., Ltd. (Jiangsu, China).

Sample preparation

Sericite with 1% (w/w) CA was mixed in a high-speed mixer for 5 min. The HDPE composite was prepared through the coextrusion of HDPE with 30% (w/w) treated sericite in a twin-screw extruder

TABLE I
Components and Physical Properties of Sericite

Component	Concentration (%)
SiO ₂	69.5–79.9
Al ₂ O ₃	12.0–15.6
K ₂ O	3.29–5.55
Fe ₂ O ₃	1.68–3.22
MgO	0.15–0.66
TiO ₂	0.12–0.26
Na ₂ O	0.10–2.00
CaO	0.07–2.22
SO ₃	0.00–0.08
MnO	<0.05
H ₂ O	3.0–5.0
Physical property	
Color	Gray-white
Shape	Lamella
Width/height ratio	40–80
Relative density	2.7–3.1
pH	6–7
Specific surface area	$9.938 \times 10^5 \text{ m}^2/\text{m}^3$

at 180–190°C. The aforementioned composite was then (1) hot-pressed at 170°C into about 120- μm -thick films and (2) injected into bars 3.2 mm thick. The natural weathering of the films and bars was carried out outdoors for 180 days (May 2004 to October 2004) according to the national standard (GB3681). The samples were placed on a plastic shelf at about 30° to the horizon to make sure that the sunlight was perpendicular to the surface of the samples.

Characterization

The oxidation degree of a composite film was monitored at a certain time interval with a Nicolet (USA), 560 Fourier transform infrared (FTIR) spectrometer. To minimize errors from the sample thickness, the 2019-cm⁻¹ peak, which was attributed to the combination of 1300 and 720 cm⁻¹, was selected as an internal reference in this study.

The carbonyl index (CI) was defined to show the oxidation degree of a sample:

$$\text{CI} = A_{\text{C=O}}/A_{2019} - \text{CI}_0 \quad (1)$$

where $A_{\text{C=O}}$ and A_{2019} are the absorbances of the carbonyl group and the reference, respectively. The peak area of the carbonyl group was determined in the range of 1800–1670 cm⁻¹. CI_0 is the original carbonyl index in the sample. Because some CAs have characteristic bands in the carbonyl region, the original CI is subtracted to remove the influence of the original functional groups. Therefore, the result stands only for the changes that happen during natural aging.

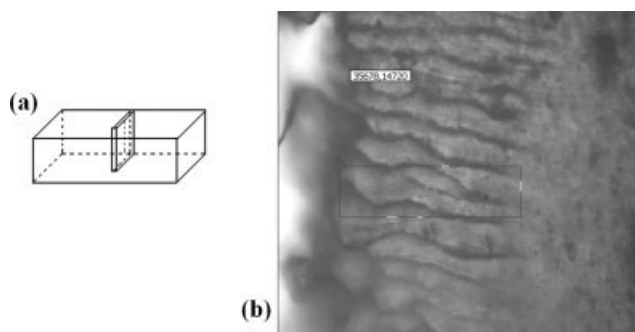


Figure 1 (a) Scheme of a test bar for FTIR microscopy measurements along the dotted line and (b) general view of a section in a test bar after 180 days of exposure (the left side is the surface).

The crystallinity (X_c) was estimated from FTIR spectra with Zerbi et al.'s equation:²⁰

$$X_c = 1 - \frac{(1 - I_a/I_b)/1.233}{1 + I_a/I_b} \quad (2)$$

where I_a and I_b are the absorbances of the peaks at 730 and 720 cm^{-1} , respectively. The constant 1.233 corresponds to the relations of the intensity bands of fully crystalline HDPE.

Sections of about 100 μm , perpendicular to the surface, were obtained with a microtome from the test bars. Figure 1(a) shows this kind of section, in which a degradation zone is optically detected close to the surface [Fig. 1 (b)]. The degradation profile versus the depth was determined with FTIR spectroscopy (IR-Prestige, Shimadzu, Japan) with an FTIR microscope accessory (AIM 8800, Shimadzu). The spectra were obtained through the averaging of 50 scans in the range of 4000–700 cm^{-1} . The CI was defined as in eq. (1).

The morphology of the film surfaces and cross sections of standard samples before and after exposure was observed with SEM (S-450, Hitachi, Japan) in the secondary electron mode at 15 keV. The samples were gold-coated before the observation.

The UV spectra of samples were collected with a Shimadzu UV 2100S ultraviolet–visible spectrometer in the range of 190–800 nm (Japan).

RESULTS AND DISCUSSION

Natural weathering behavior

Figure 2(a) shows the spectra of HDPE/sericite composites with different CAs before exposure. In the spectra of the composites after exposure [Fig. 2(b)], distinct carbonyl groups (top at 1716 cm^{-1}) appeared, with different intensities according to the different CAs. Comparing the locations of the carbonyl bands in HDPE/sericite composites with or

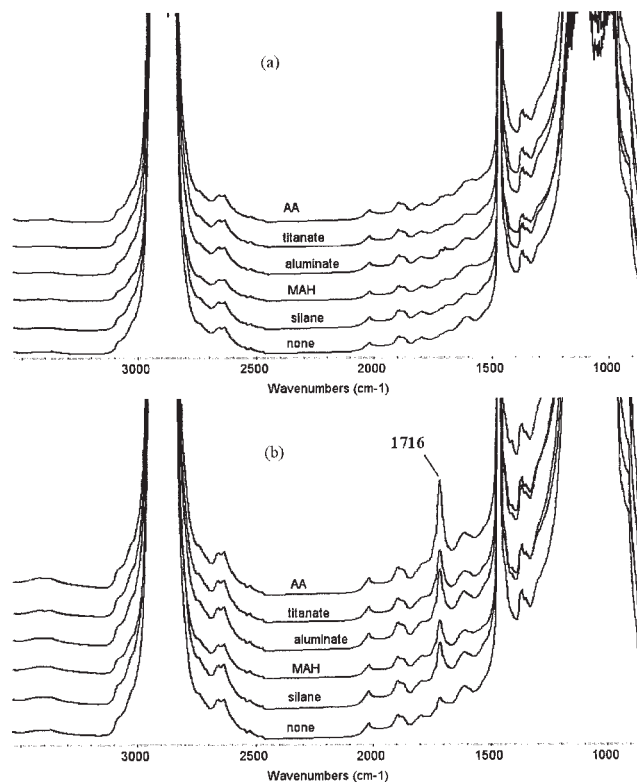


Figure 2 FTIR spectra of HDPE/sericite composites with different CAs. (a) before exposure and (b) after exposure.

without CA, one could find that although the composites with different CAs had various oxidation degrees, the band positions and shapes were similar. This demonstrated that the treatments with different CAs did not change the oxidation products of the HDPE/sericite composites.

The CI curves versus the exposure time in Figure 3 showed substantial differences within the composites with different CAs. The greatest concentration of

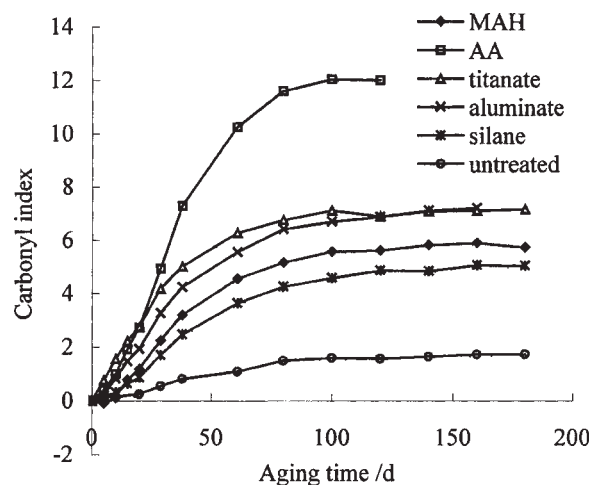


Figure 3 Change in the CI with time in HDPE/sericite composites with different CAs during exposure.

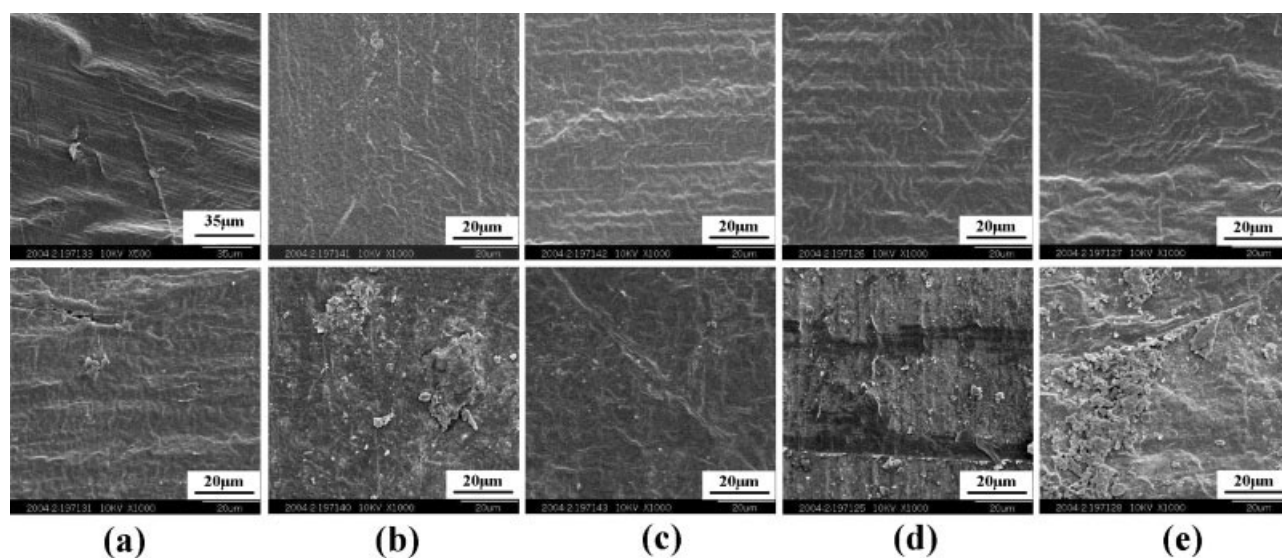


Figure 4 Film surface morphologies of HDPE/sericite composites with (a) no CA, (b) MAH as a CA, (c) titanate as a CA, (d) aluminate as a CA, and (e) silane as a CA before and after natural photooxidation. The upper photographs were taken before the exposure. The lower ones were taken after the exposure. The HDPE/sericite/AA film was broken into pieces and lost, so its surface morphology was not available.

carbonyl groups was registered for an AA-treated composite that fractured after 120 days of exposure. The untreated one yielded the smallest value of CI, whereas other CA-treated composites gave intermediate ones. Although the titanate-treated composite showed behavior similar to that of the AA-treated composite at the early stage of exposure, its final oxidation degree was much lower, roughly the same as that of the aluminate-treated composite. The MAH- and silane-treated composites, in turn, had lower oxidation degrees. For all the composites, there was no obvious induction time observed.

A higher oxidation degree does not always correspond to a more seriously damaged surface. Because the film surfaces were directly exposed to UV light, it is reasonable to assume that a highly oxidized film would have a seriously damaged surface. Nevertheless, the experimental results did not support this assumption. In Figure 4, the surface morphologies of the HDPE composite films before and after exposure are presented. The film surfaces before exposure were smooth. Some wrinkles on them were caused by the hot-pressing procedure. For the films after exposure, the surface morphologies showed considerable differences. For example, in titanate- and aluminate-treated HDPE/sericite, although the oxidation degrees were similar, their surface damages differed completely. The surface of titanate-treated HDPE/sericite was relatively smooth after exposure, whereas on that of aluminate-treated HDPE/sericite, there were deep cracks. On the surface of silane-treated HDPE/sericite, there were quite a few particles dispersed, although the final oxidation degree

of this composite was relatively low. These particles might have been due to the chain scissions of HDPE, which caused a lot of fragments on the surface, or these particles were filler particles that appeared on the surface after the loss of surface fragments. The reason for the discrepancy between the oxidation degree and the surface damage has been discussed elsewhere.⁹

It is accepted that an oxidation reaction prefers to occur in the amorphous phase or along the boundary of the crystal phase.²¹ In the crystal phase, oxidation is quite difficult because of the rather low oxygen diffusion. Therefore, it is reasonable to propose that a sample with high crystallinity may have high stability. In our previous work,⁹ sericite acted like a nucleation agent and increased the crystallinity of HDPE. With CAs covering the surface of inorganic particles, this nucleation effect would change. Figure 5 shows the crystallinities of HDPE/sericite composites with different CAs before and after exposure. The MAH treatment reduced the crystallinity greatly, whereas other CAs did not influence the crystallization obviously. The crystallinities did not agree with the oxidation degree. The low crystallinity of the MAH-treated composite did not correspond to high oxidation. In contrast, although the AA-treated composite had the same crystallinity as the untreated one, it had the highest oxidation. This discrepancy suggested that the original crystallinity was not the predominant factor. After exposure, the crystallinities of all composites increased, whatever the CA was. According to White and coworkers,^{22–25} the crystallinity increment arose from the chemical

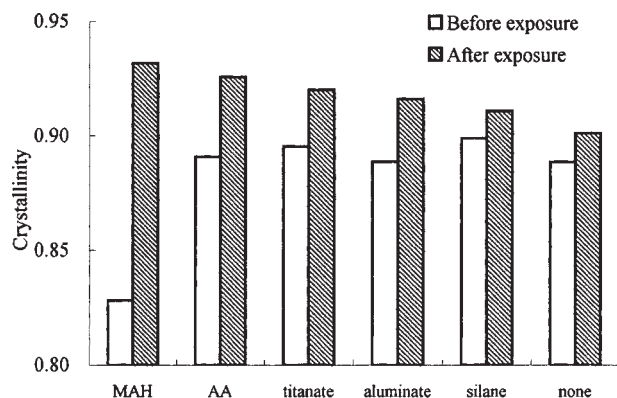


Figure 5 Influence of the CA on the crystallinity of the HDPE/sericite composite.

crystallization of small molecules that formed in the photooxidation process. Except for the MAH-treated composite, the crystallization variation of the composite correlated well with the oxidation degree and the crack formation. The AA-treated composite had a high crystallinity increment of 3.9%; the next were the titanate- and aluminate-treated composites. The silane-treated composite had a crystallinity increment similar to that of the untreated one: 1.3%. The abnormal variation of the MAH-treated composite

implied other factors during the exposure, which need further investigation in the future.

Crack and oxidation profile

In a thick sample, the oxidation reaction can go more deeply into the interior and give rise to a different behavior than that of a thin film. For example, there were parallel, comblike cracks from the surface to the interior on the cross sections of some HDPE composites after exposure.²⁶ With different CAs covering the surface of the filler particles, the appearance of the cracks showed various features. Figure 6 shows the morphologies of cross sections of HDPE/sericite composite bars with different CAs. The left edge in each picture represents the exposed surface of the standard bar. On the sectional photographs, comblike cracks formed after exposure. The average crack length and the crack density changed with the CAs. In HDPE/sericite, the cracks were nearly 200 μm long, with a smooth surface. In the treated composites, the cracks increased both in the length and in the density. In addition, more or fewer fragments dropped from the surfaces. Table II lists the crack data for the standard bars and the final CIs of the corresponding films. It is amazing that there is a

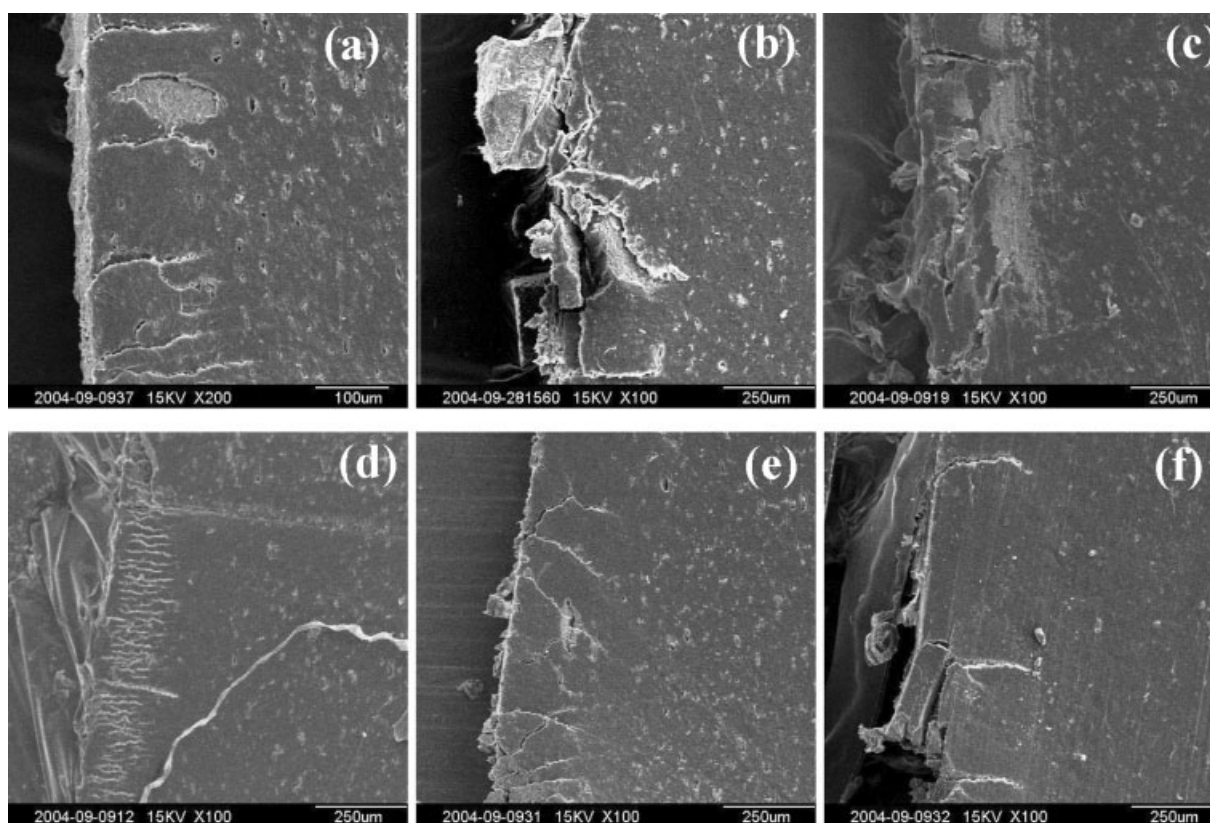


Figure 6 Morphologies of cross sections of test bars of (a) HDPE/sericite, (b) HDPE/sericite/MAH, (c) HDPE/sericite/AA, (d) HDPE/sericite/titanate, (e) HDPE/sericite/aluminate, and (f) HDPE/sericite/silane.

TABLE II
Relationship Between the Oxidation Degree and Crack Status

Sample	CI of the film after exposure	Average crack length (μm)	Average crack density (/100 μm)
HDPE/sericite/MAH	5.73	200	<1
HDPE/sericite/AA	12.01 ^a	350	<1
HDPE/sericite/titanate	7.16	175	5
HDPE/sericite/aluminate	7.20	250	2
HDPE/sericite/silane	5.04	250	<1
HDPE/sericite	1.73	185	1

^a This value was obtained after 120 days. After that, the film broke into pieces.

good consistency between the oxidation degree in Figure 3 and the crack formation. For a sample with a higher CI, the average crack length was greater, such as the AA-treated composite. For the titanate-treated composite, although its crack length was short, its crack density was quite high. As a result, its oxidation degree was also high. For an untreated one, both the crack length and the crack density were small, so the final oxidation degree was low.

With cracks propagating from the surface to the interior, it is reasonable to presume an oxidation profile along the depth in a thick sample. By IM analysis, the oxidation profiles of the composites were obtained through the line mapping of the cross section from the surface to the interior. The oxidation profiles versus the depth for HDPE/sericite composites with different CAs are plotted in Figure 7. At the surface of the test bar, the formation of the carbonyl group (top at 1716 cm^{-1}) was the highest. Then, it declined gradually along the depth. The AA-treated sample had the greatest carbonyl formation at the surface in comparison with the other composites. Its CI decreased steeply from the surface to the depth of about $200\ \mu\text{m}$. After that, the CI remained constant at a low oxidation level. For other composites, the behaviors were similar, whereas the maximum CI was obtained not at the

surface but at the subsurface layer. The oxidation level reached an extreme at about $75\ \mu\text{m}$. Then, it went down gradually and reached nearly zero at the depth of $300\text{--}400\ \mu\text{m}$.

Effects of sericite and the CAs

Sericite has a layer structure. It contains two silica tetrahedral sheets and an aluminum hydroxyl octahedral sheet between them. Sericite is known to have a UV-shielding effect, and the H_2O crystal between the silicate layers has an interference effect on the light.⁶⁻⁸ However, in the natural aging of the HDPE/sericite composites, sericite acted like an oxidation catalyst. The UV spectra of sericite, HDPE, and an HDPE/sericite composite are plotted in Figure 8. Sericite reflected UV light above $400\ \text{nm}$. For UV light of less than $400\ \text{nm}$, the reflectance of sericite was quite low. Consequently, the HDPE/sericite composite had much higher absorbance of UV light, especially in the region of less than $400\ \text{nm}$. In HDPE, sericite might act like a sensitizer for the photooxidation reactions. This catalyst effect would be responsible for more bond scissions in polyethylene molecules and thus lead to higher oxidation than HDPE itself. Sericite also has active oxygen atoms in the corners of its crystals,⁷ which might also acceler-

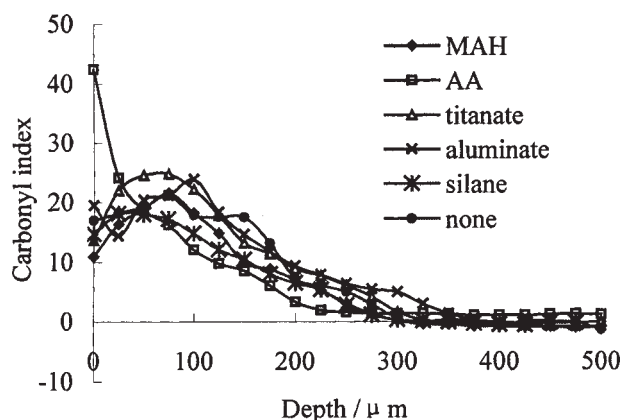


Figure 7 Oxidation depth profiles of HDPE/sericite composites with different CAs.

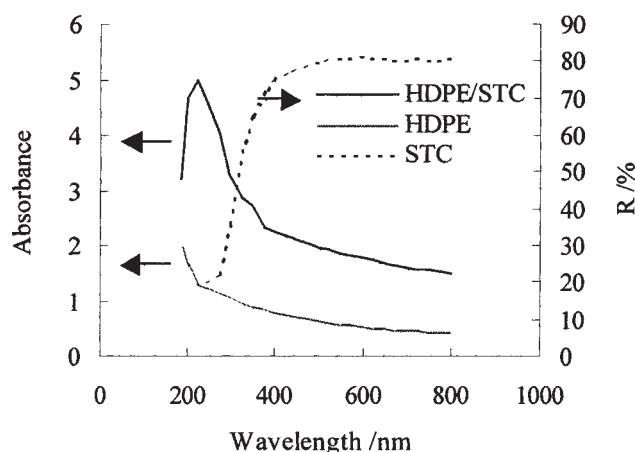


Figure 8 UV spectra of sericite (STC), HDPE, and an HDPE/STC composite.

ate the oxidation of HDPE. In addition, sericite flakes with sharp edges and corners act like a lot of stress-focusing positions, which help the initiation of the cracks under environmental stress.

CAs play a very important role in polymer composites. As mentioned previously, a CA is like a bridge connecting an immiscible matrix and inorganic particles. With their help, filler particles can disperse evenly in the matrix, and the interfacial cohesion of these two are improved. With a strong interfacial interaction, the mechanical properties, especially the toughness of the composite, will experience a prominent improvement. There are thousands of reports concerning the effects of CAs on the mechanical properties of polymer composites. However, there is little work reported on their effect on aging behavior.

CAs can make at least three changes in the aging behavior of polymer composites:

1. They help to decrease the aggregation of filler particles, which always serve as impurities in composites.
2. They cover the surface of inorganic particles. This shields the catalyzing effect of these particles and smoothes the sharp edges or angles of irregular particles, which easily induce cracks.
3. They serve as chromophores themselves because of their functional groups.

In Figure 6, one can find that there are many voids in a sectional photograph of HDPE/sericite caused by the interfacial decohesion of filler particles from the matrix after exposure. In contrast, there are fewer voids in the sections of treated HDPE/sericite composites, and this shows the improved interfacial cohesion. However, the better interfacial cohesion does not correspond to higher stability. The untreated composite had the lowest oxidation degree. The average crack length was also the shortest. The bridge effect and coverage effect were not the main reasons for the catalyzing effect of CAs on the photooxidation degradation of HDPE/sericite.

There are oxygen-containing functional groups in CAs, such as carboxylic groups in MAH and AA, double bonds in AA, ester groups in titanate and aluminate, and amino groups in silane. These groups show some traces in the spectra of some treated HDPE/sericite composites, especially in the titanate-treated one (in Fig. 2). During the photooxidation process, they serve as chromophores to initiate photooxidation reactions. Because of the different reactivities of different functional groups, they show different influences on the oxidation. For example, both

carboxylic groups and double bonds in AA can absorb UV light and initiate a photooxidation reaction. Hence, the oxidation degree of the AA-treated HDPE/sericite composite remained the greatest throughout natural aging.

CONCLUSIONS

Sericite is a promising reinforcing filler with a high aspect ratio. For some polymers such as PP, it can also serve as a light stabilizer. In HDPE, however, sericite plays a reverse role. The oxidation of an HDPE/sericite composite is faster than that of HDPE, and the final CI is greater as well. This effect is due to the excessive absorbance of UV light by sericite, and the active oxygen atoms at the corners of the sericite crystals may also make some contribution. Apart from this, because inorganic fillers may influence the crystallization behavior of the matrix and the internal stress distribution and thus influence crack formation during natural aging, further research will be carried out.

CAs are often used to treat sericite particles before blending to improve their interfacial cohesion to the matrix, and they likewise have great effects on the photooxidation of HDPE. All of them, especially AA, accelerate the formation of oxidative products. This is mainly because of light-active functional groups such as carbonyl groups, carboxylic groups, and double bonds in CAs.

Thick samples have a particular aging behavior with respect to the depth. On sections of HDPE/sericite composites after natural exposure, more or less parallel cracks of more than 150 μm form with different densities. The formation of cracks is also dependent on CAs. Comparing the crack formation and oxidation profile in a composite, we find that longer and/or denser cracks give rise to higher oxidation degrees. This is easy to understand because more or longer cracks supply more tunnels for oxygen to disperse into the interior and more oxidation is possible.

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