

Degradation of Nano ZnO-Glass Fiber-Unsaturated Polyester Composites

Guirong Peng, Qingshan Li, Yanling Yang, Haifeng Wang

National Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, People's Republic of China

Received 26 November 2007; accepted 2 January 2009

DOI 10.1002/app.29988

Published online 2 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Degradation behavior of ZnO-glass fiber-unsaturated polyester composite under exposure to a metal halide lamp is investigated by means of DSC and FTIR. The FTIR results show that the UV photons can increase the carbonyl group on the surface, but ZnO can decrease the carbonyl content and further contribute to the breaking of single bond of carbon to oxygen on the surface. All of the results indicate that for pure unsaturated polyester under the UV exposure in air, the major reaction is photo-initiated oxidation, whereas for the composites with ZnO, decarbonylation is the major effect. In addition, when the content of

ZnO is not higher than 4 wt %, the composites are still transparent, and its effects on the crosslinking process and thermal stability are insignificant. Thus, ZnO can be used as a stabilizer of unsaturated polyester for the glass fiber reinforced polymer industry. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2128–2133, 2009

Key words: nano ZnO; composite materials; unsaturated polyester; Fourier transform infrared spectroscopy (FTIR); thermogravimetric analysis; photoinitiated oxidation; photo aging

INTRODUCTION

Thermosetting resins and their composites are widely used in many areas due to their superior properties and lower price. However, the environmental degradation of polymer materials limits their service life; solid waste produced by polymers is difficult to be recycled, which also limits their use.^{1–6} Some methods, such as surface coating,^{7,8} surface film layers,^{9,10} and antidegradation additives,^{11–13} have been used to impede the environmental degradation of thermosetting resins. Though some good results were gained,^{11–15} there is a limitation with these methods. Organic additives are easy to lose and less effective for thermosetting resins.^{11–13} Most of the surface coating and surface film layers that are applied nowadays are easily peeled off and hence lose their protective effects.

Inorganic particles are also added to protect resins from environmental degradation; however, the addition of common inorganic particles in thermosetting resin generally results in a decrease in strength and transparency. Nanoparticles usually have a more active surface and are easily bonded to the resins with sufficient strength and thus do not decrease the materials' strength. The effects of nanoparticles on

strengthening and toughening in thermosetting resin composites have been reported extensively.^{16–25}

Nano ZnO is superior due to its strong absorption ability.^{23,26} It can be used to protect matrix resins from environmental degradation. Moreover, its small diameter and relative low quantity addition would have very little influence on materials' transparency²⁶ and increase the toughness and antibacterial ability of materials. In addition, the materials of surface layers are expensive and are supplied by only a limited number of manufacturers,^{7–10} whereas the price of nanoparticles is decreasing with the development of technology. Therefore, the application of nano ZnO in the stabilization of unsaturated polyester will benefit the glass fiber reinforced polymer industry. Thus series investigations on the effects of nano ZnO on unsaturated polyester are carried on. Previous paper,²⁷ showed that under exposure to the metal halide lamp, nano ZnO can significantly delay the UV degradation process of the matrix resin and can also increase the impact strength of the composites under the experimental conditions and can hinder crack growth and induce more cracks; when the content of ZnO reaches 6 wt %, the impact fracture mechanism changes abruptly and plastic deformation appears. The results indicate that the proper content of ZnO added into unsaturated polyester could prolong the durability and lessen the rejected rate of transparent glass fiber-polyester composites. In the paper, with FTIR analyses and more DSC results, the degradation

Correspondence to: G. Peng (gr8599@yahoo.com.cn).

mechanism of ZnO-glass fiber-unsaturated polyester composite under exposure to a metal halide lamp and the effects of ZnO on the thermal property are studied further.

EXPERIMENTAL

Unsaturated polyester number 193 with an acid number of 40 ± 10 mg KOH/g (number average molecule weight is 1400 g/mol) and glass fiber tabby cloth with 30 mm width and 0.3 mm thick were provided by Yaohua GFRP of Qinhuangdao in China and were used as received. Nano ZnO particles with an average diameter of 30 nm were from Anhui University of Technology, Ma An Shan, China.

KH570 was used to modify nano ZnO, which is γ -methacryloxypropyltrimethoxysilane. In water or alcohol, it hydrolyzes to trihydroxyl compounds with one unsaturated bond. The hydroxyl can bond with inorganic materials and the unsaturated bonds can react with other unsaturated bonds in polyester and styrene.

Nano ZnO was dried at 110°C for 24 h to remove adsorbed water. The dried nano ZnO was ultrasonicated for 10 min in analytical pure ethanol and for another 20 min after the addition of coupling agent KH570 (analytical pure, Damao chemical reagent factory of Tianjin in China). After 1 h, the mixture was filtrated and dried at 60°C for more than 24 h. The concentration of KH570 is 5 wt % of ethanol and 2 wt % of ZnO. The dried filtrate was ground to power in mortar. Figure 1 is the FTIR spectra of ZnO before and after modified with KH570. It can be seen that after modification with KH570, new peaks appear at 2880, 2958, 1718, and 1251 cm^{-1} , and the intensity at 1100 cm^{-1} increases, which demonstrates that some KH570 has reacted with the ZnO particles.

The composite is made with the hand lay-up technique, crosslinked with BPO (benzoyl peroxide, initiator of chain polymerization in unsaturated materials) (1 wt % of resin, analysis pure, Tianjin Kermel Chemical Reagent, China) and *N,N*-dimethylaniline (0.01 wt % of resin, as activator) at room temperature for 24 h. First, the glass fiber and the treated ZnO were mixed with the unsaturated polyester and then the initiator and activator were added. The fiber content in the composite was about 35 ± 5 wt % (calcination method). The composite plate was cut to 60 mm \times 6 mm \times 3 mm with a diamond saw for the environmental degradation and bending test. Samples for DSC and FTIR analyses were cut from surface skin in the middle of the samples.

The three-point bending test was carried out at 2 mm/min with a span distance of 40 mm at room temperature by using an AG-101TA type machine made by Jinjian of Chende, Hebei, China (referred to

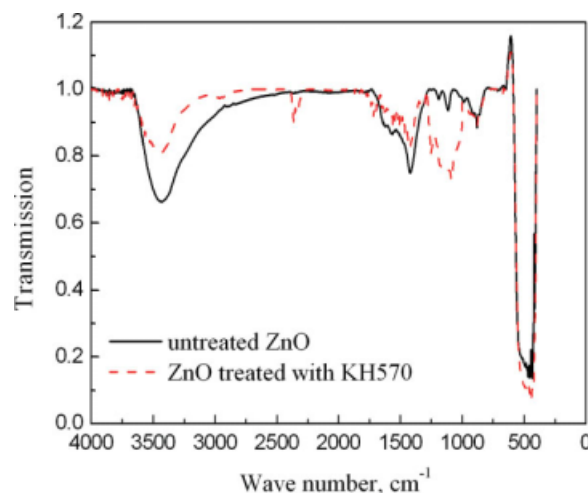


Figure 1 FTIR spectra of ZnO before and after modified with KH570. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as GB1447-78). At least four to six specimens were tested for each testing point.

The composite samples were placed at 500-mm distance from a 400-W metal halide lamp (MIWF330/400s) for the UV stability test. Both samples and lamp were placed in a ventilated chamber.

DSC (STA449C of German NETZSCH) was carried out from room temperature to 700°C in Ar atmosphere. The heating rate was 15°C/min. The sample weight was about 10 mg.

FTIR was carried out with KBr pellet at E55+FRA106 of Bruker, Germany, from 400 to 4000 cm^{-1} with resolution of 0.5 cm^{-1} and precision of 0.01 cm^{-1} . The samples were from the exposure surface.

RESULTS AND DISCUSSION

Bending strength ratio of the exposed to original unexposed samples of the same composition for ZnO-glass fiber-unsaturated polyester composites is shown in Figure 2. It demonstrates more clearly that the samples with ZnO can keep more strength than that without ZnO and hinder the effect of light on composites as expected. However, when the content of ZnO is higher than 4 wt %, the agglomeration of nanoparticles hinders the performance of nano ZnO and the curve change is slower compared with that of 2 wt %.

The TG curves of ZnO-glass fiber-unsaturated polyester composites are shown in Figure 3. It can be seen that for the sample without ZnO, a 5% weight loss is observed in the temperature range of 200–250°C, and the remaining weight is up to 337°C and then decreases with further increase of temperature. The max rate of weight loss is at 380°C. However, for the samples with the addition of ZnO particles in composites, the initial decomposition temperature is at about 250°C. It can be considered

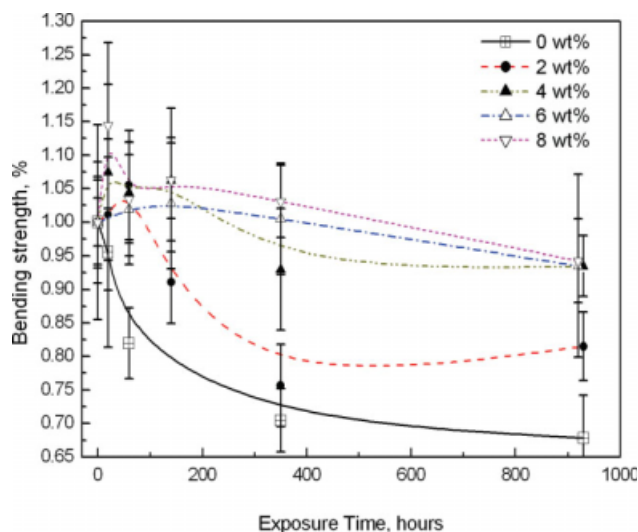


Figure 2 Bending strength ratio of the exposed to the unexposed for ZnO-glass fiber-unsaturated polyester composites with exposure time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as a two-stage decomposition. The transitional point is at about 350°C (see Fig. 4). For the first stage, decomposition rate is slower compared with that of the second stage. The max decomposition rate is at 380°C also. For the pure unsaturated polyester composites, there is a second phase transition at 165°C, max decomposition peak at 384°C, and a small peak at 460°C. For the composites with 4 wt % ZnO, it changes only in the intensity of the peak at 384°C (see Fig. 5). For the samples with ZnO more than 4 wt %, the second phase transition changes to an exothermic peak and moves to lower temperatures at about 135°C, which might result from the post cross-linking; a new peak appears at 320°C, and the area

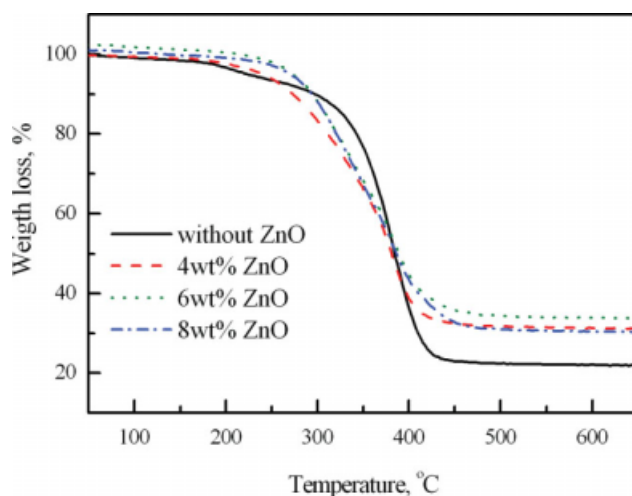


Figure 3 TG curves of ZnO-glass fiber-unsaturated polyester composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

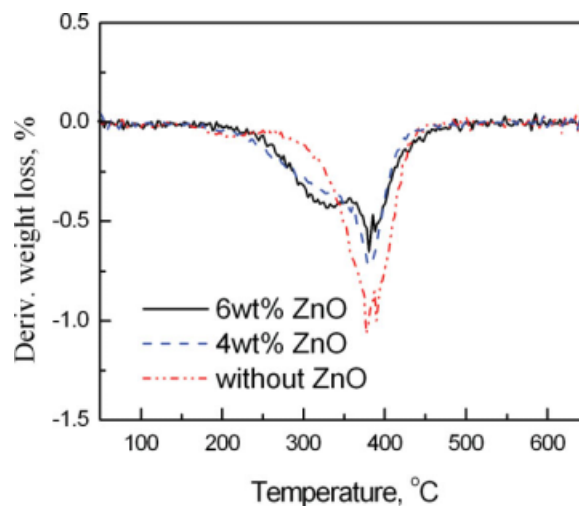


Figure 4 Differential TG curves of ZnO-glass fiber-unsaturated polyester composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the peak at 384°C decreases, which is consistent with the results of TG analyses. All of these results indicate a new decomposition mechanism for the samples with enough ZnO.

ZnO crystal is a kind of amphoteric compound and has anionic and cationic polar surfaces.²³ This structure ensures that ZnO could react with a negative group to form a catalyst complex and catalyze the decomposition. Thus the carbonyl group could be more easily broken and the decomposition of the unsaturated polyester composites could take place at a lower temperature, and an endothermic peak appears at lower temperatures, which is the new decomposition mechanism.

The peak at 135°C might result from the post cure, which seems to indicate that ZnO prolongs the

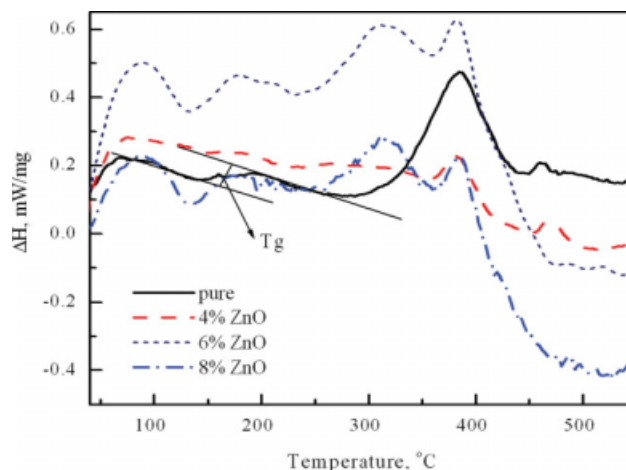


Figure 5 DSC plots of ZnO-glass fiber-unsaturated polyester composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

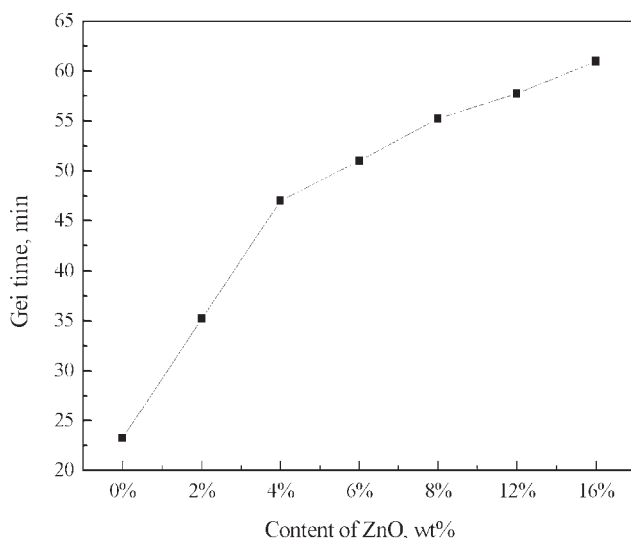


Figure 6 Gel time for unsaturated polyester with various contents of ZnO at 50°C.

crosslink of the unsaturated resins. To verify the influence of ZnO on the polyester, the gel time is tested at 50°C, in which the gel time is the time period from the time that BPO (0.1 wt % of the resin) and *N,N*-dimethylaniline (0.01 wt % of the resin) mixed with the resin to that continue thread can be drawn from the resin mixture. As shown in Figure 6, the gel time period for unsaturated polyester is increased with the content of ZnO. However, UV photon could induce the unsaturated polyester further crosslinked when the samples are irradiated for more than 40 h, as can be seen in Figure 7.

The second phase transition temperature at 160°C is too high for unsaturated polyester, but for the high crosslinking structure and the physical crosslinking of particle ZnO in the matrix resins, the temperature is possible.

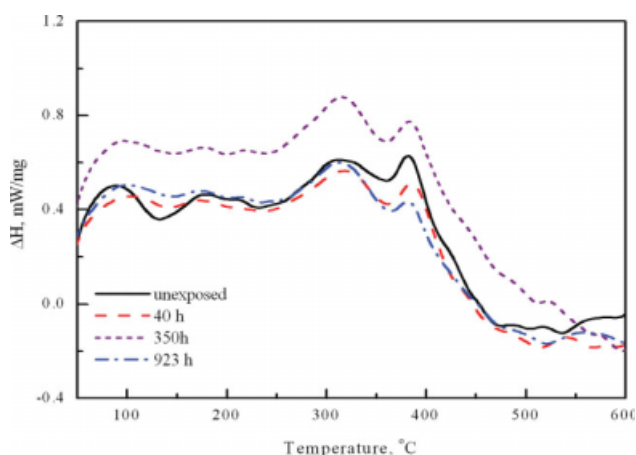


Figure 7 DSC plots of glass fiber-unsaturated polyester composites with 6% ZnO after exposure for various times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

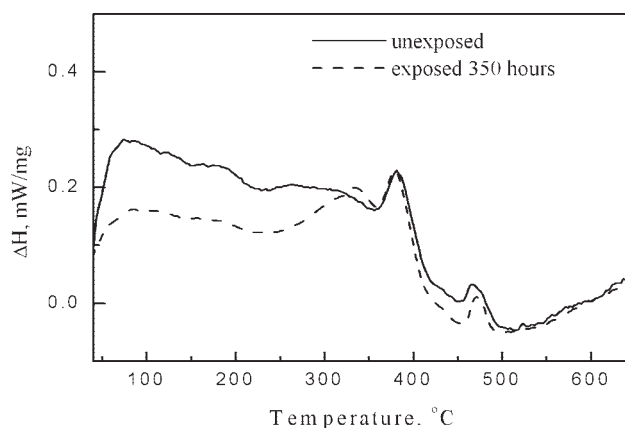


Figure 8 DSC plots of glass fiber-unsaturated polyester composites with 4% ZnO before and after exposure for 350 h.

The relative intensity ratio of the new peak around 320°C to the peak at 380°C is increased with the exposure time, as shown in Figure 7, which indicates that catalysis of ZnO to the decomposition of unsaturated polyester can be further activated by the survival active center after lamp exposure, or the structure after exposure could be more easily decomposed, which gives the endothermic peaks at 320°C. The area ratio of peaks at 320–380°C increases with the content of ZnO, which indicates that the new decomposition is not a result of the changed structure but is due to the existing of ZnO (Fig. 5). Therefore, it is believed to be the survival active center after lamp exposure, which leads to the increase of the relative intensity ratio of the new peak at around 320°C to the peak at 380°C.

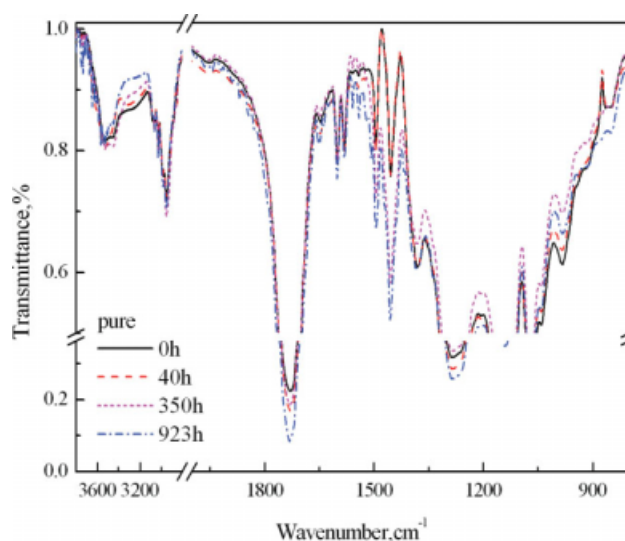


Figure 9 FTIR spectra of pure unsaturated polyester before and after exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

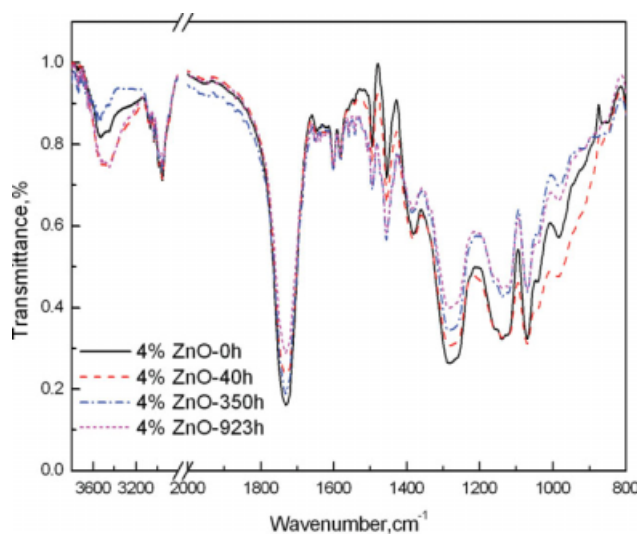


Figure 10 FTIR spectra of glass fiber-unsaturated polyester composites with 4 wt % ZnO before and after exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For the glass fiber-unsaturated polyester composite with 4 wt % ZnO (see Fig. 8), there is no significant change in the DSC plot compared with the samples without ZnO before exposure to lamp; but after 350 h of exposure, a new peak at 330°C appears, which further confirms the activation of UV exposure on catalysis of ZnO to polyester degradation.

Figures 9–11 are FTIR spectra of the composites before and after exposure to lamp. The samples are acquired on the irradiated surface. Tables I–III are the relative intensity of the absorption peak vs. exposure time. The intensity is normalized referring to

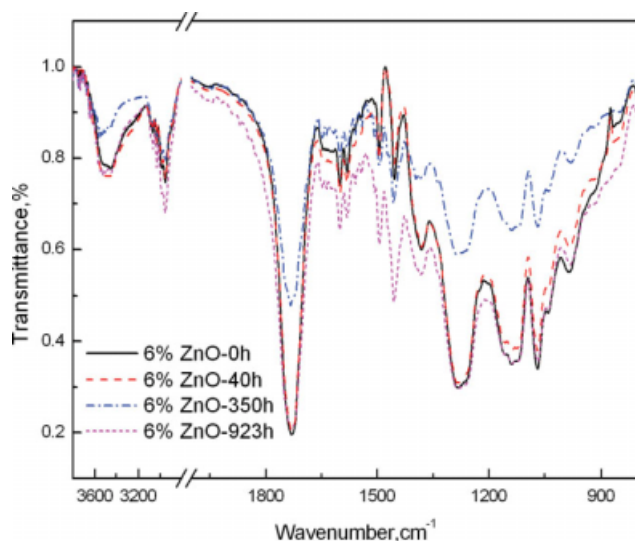


Figure 11 FTIR spectra of glass fiber-unsaturated polyester composites with 6 wt % ZnO before and after exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Changes of Absorption Peak Intensity with Exposure Time for Glass Fiber-Unsaturated Polyester Composites without ZnO (From FTIR, Internal Normalized to the Peak Intensity at 3063 cm⁻¹ and that of Before Exposure)

Wave number (cm ⁻¹)	0 h	40 h	350 h	923 h
1730	1.00	1.12	1.06	1.17
1600	1.00	1.08	1.00	1.12
1454	1.00	1.04	1.74	1.96
1068	1.00	1.05	0.93	1.00
981	1.00	0.98	0.79	0.86

the peak of 3063 cm⁻¹ and then is normalized referring to the intensity of every peak before exposure. It can be seen that for the sample without ZnO, the peak at 1730 cm⁻¹ is increased and the peak at 1068 cm⁻¹ changes slightly with the time of irradiation. For the sample with 4 wt % ZnO, both of these two peaks decrease with the increase of irradiation time, but not significantly. For that with 6 wt % ZnO, both of these two peaks decrease obviously. The different trends of the two peaks with irradiation time could be considered resulting from the addition of ZnO. That is to say, on the surface, ZnO could accelerate the process of decarbonylation and further break of single bond of carbon to oxygen.

The overall effects of ZnO on polyester could be summarized as follows: First, it can prolong the gelation time period and decrease the crosslink density of the polyester under ambient temperature, but the unsaturated polyester could be further cross-linked by UV photons; Second, ZnO can catalyze the decomposition of polyester and give the new endothermic peak at 320°C, consequently decrease the initial decomposition temperature, and reduce the intensity of the decomposition at 380°C. The new decomposition at 320°C could be activated by the UV photon. The FTIR results show that the UV photons could increase the carbonyl group on the surface, but ZnO could decrease the carbonyl content and further contribute to the breaking of single bond of carbon to oxygen on the surface. All of these indicate that for epoxy without ZnO under UV exposure

TABLE II
Changes of Absorption Peak Intensity with Exposure Time for Glass Fiber-Unsaturated Polyester Composites with 6 wt % ZnO (From FTIR, Internal Normalized to the Peak Intensity at 3063 cm⁻¹ and that of Before Exposure)

Wave number (cm ⁻¹)	0 h	40 h	350 h	923 h
1730	1.00	1.02	0.70	0.79
1600	1.00	1.11	0.82	1.11
1454	1.00	0.89	1.32	1.67
1068	1.00	0.97	0.58	0.79
981	1.00	0.92	0.51	0.78

TABLE III
Changes of Absorption Peak Intensity with Exposure Time for Glass Fiber-Unsaturated Polyester Composites with 4 Wt % ZnO (From FTIR, Internal Normalized to the Peak Intensity at 3063 cm⁻¹ and that of Before Exposure)

Wave number (cm ⁻¹)	0 h	40 h	350 h	923 h
1730	1.00	0.90	1.16	0.94
1600	1.00	1.00	1.16	1.09
1454	1.00	1.21	1.80	1.64
1068	1.00	1.01	0.98	0.91
981	1.00	1.20	0.81	0.87

in air, the major reaction might be photoinitiated oxidation, whereas for the composites added of ZnO, the decarbonylation might be the major effect.

As a kind of amphiprotic compound, ZnO crystal has anionic and cationic polar surfaces and can react with negative group to form complex and absorb most of the energy of UV photon and induce the obvious change on the surface. In addition to the physical absorption of ZnO, most of the energy of light is absorbed and depleted on the surface skin. Thus the matrix could be protected from the photoinitiated oxidation. The samples with ZnO show higher strength than that without ZnO after exposure.

CONCLUSIONS

ZnO can retard the decrease in strength for the composites under lamp exposure. DSC analyses show a new endothermic peak at about 320°C, which increased with the content of ZnO and the exposure time. It is considered that the new decomposition results from decarbonylation catalyzed by ZnO, and the UV exposure further activated the catalyzed decarbonylation. The FTIR results show that the content of carbonyl group on the surface is increased under UV exposure, but ZnO could decrease the carbonyl content and further contribute to the breaking of a single bond of carbon to oxygen on the surface. All of these results indicate that for pure unsaturated polyester under the UV exposure in air, the major reaction might be photoinitiated oxidation, whereas for the composites added of ZnO, decarbonylation is the major effect.

Since UV is absorbed and depleted on the surface skin, the matrix of the composites is free of UV influence, which results in the composites being more stable to lamp exposure. ZnO could benefit from the resistance of the glass fiber-unsaturated polyester composites to UV exposure but decrease the thermo-stability, and the decrease is not serious. In addition, when the content of ZnO is not higher

than 4 wt %, the composites are still transparent. Thus, ZnO can be used as a stabilizer for unsaturated polyester for glass fiber reinforced polymer industry.

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