THE EFFECTS OF ULTRAVIOLET RADIATION (UVR) IN POLYMER-BASED COMPOSITES

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Abstract
A comparison test was conducted on the tensile properties of zinc oxide (ZnO)/glass fibre reinforced unsaturated polyester (GF/UP) composites underwent accelerated continuous and cyclic UVR exposure. The degradation rate given by the change in Young's Modulus of 6 wt.% 100nm undoped ZnO/GF/UP composites underwent continuous UVR exposure is 2 times faster than cyclic exposure. Accelerated continuous and accelerated cyclic UVR exposure tests have been utilized to study the UVR effects in materials. However, there are a limited research worked on the interpretation of the service life of polymer-based composites in terms of UVR degradation. Furthermore, implementing ZnO into polymer is a solution for protecting the core composite from UVR degradation. A top layer of ZnO/epoxy/hollow glass fibre (HGF) is introduced, 4 wt.% ZnO is tested as an optimum amount in terms of UVR absorbability and stress transfer ability. It is suggested that the problem of particle dissolution and wearing out could be solved by the newly-configured layer.

1. Introduction

Ultraviolet radiation (UVR) causes harmful effects to polymer-based materials. Every 1000m increases in altitude, 10-12% increases in UVR intensity. When an aircraft flies in stratosphere level of 8-16km high above the Earth surface, the aircraft fuselage experiences a high UVR intensity. It is seriously damaging, especially nowadays, the fuselage of new generation of aircrafts, A350 and B787, are built by using fibre reinforced polymer composites (FRPs). In addition, there is a dramatically increase of using the composites on the outer surface of automobiles and buildings due to their high stiffness or strength to weight ratio, and it results in reducing the use of nonrenewable fuel. Most critically, the depletion of ozone layer above the Earth in areas of South Pole, Australia, New Zealand, Chile, Argentina and South Africa, which is responsible for UVC absorption, has been becoming serious.

Testing the mechanical properties of materials in terms of UVR degradation is becoming a concern in civil engineering, as construction materials are normally required to maintain their serviceability for 50 years. Investigations are conducted on the influence of UVA degradation in the mechanical performance of zinc oxide (ZnO)/glass fibre reinforced unsaturated polyester (GF/UP) composites and ZnO/shape memory polymers (SMPs).

The degradation rate of 6 wt.% 100nm undoped ZnO/GF/UP composite underwent continuous UVA exposure is 2x faster than cyclic exposure (Fig. 1). The effects of UVR degradation in 6 wt.% 100nm undoped ZnO/GF/UP and EP are also compared [1].

After UVA exposure, the surface of epoxy-based SMP (EP-SMP) is softened (Fig. 2) and styrene-based SMP (S-SMP) is hardened (Fig. 3) which the results correlate with the scission and the building of crosslinks respectively. The softened EP-SMP shows a decrease (Fig. 4) and the hardened S-SMP shows an increase (Fig. 5) in UVR absorbability. The UVR absorbability of EP- SMP and S-SMP are found to be dependent on the bonding strength and the molecular chain density. And for these two SMPs with 2mm thickness, 4 wt.% 100nm undoped ZnO is confirmed to be an optimum amount for the composite to achieve a whole range of UVR absorbability (Fig. 6) and a sustained mechanical properties [2].

In commercial industry, UVR coating is commonly used for the protection of materials from UVR degradation. However, the coating is easily scratched off and the embedded nanoparticles may diffuse out from micro-cracks induced by UVR degradation or dissolve out under physical action, chemical and water extraction. To solve the problem of particle dissolution and wearing out, lower the UVR degradation rate and maintain the mechanical properties of FRPs under UVR exposure, a ZnO/epoxy filled hollow glass fibre (HGF) layer is proposed to be the top layer for UVR absorption and UVR degradation protection in the core.

From experiments, 4 wt.% of 100nm undoped ZnO/epoxy is proven as a good candidate to be filled into HGF in terms of UVR absorbability [3]. Good UVR absorbability evaluated by UV-vis spectrophotometer (Fig. 7) is confirmed to be related to the even dispersion of ZnO nanoparticles observed under microscope (Fig. 8) and the lower viscosity properties of ZnO/epoxy fluid measured using rheometer (Fig. 9) [4]. The silane-doped ZnO particle is found to be ineffective for UVR absorption. It is suggested that the silane surface refracts and blocks UVR to penetrate into ZnO atom for energy dissipation.

A theoretical model (Eq. 1), considering the initiation of fibre debonding of ZnO/epoxy/HGF, is developed to study the stress transfer ability of the composite system (Fig. 10). The content of ZnO nanoparticles (Fig. 11), the length of HGF (Fig. 12) and the shear modulus (Fig. 13) and the thickness of adhesive layers (Fig. 14) are shown as taking the major responsibilities for the stress transfer ability of the composite system. From theoretical and experimental analyses, 4 wt.% ZnO/epoxy is an optimum solution to be filled into HGF as a protective layer for core FRPs from UVR degradation in terms of stress transfer ability and UVR absorbability [5].

## 2. Guidelines

2.1. Figures and Tables

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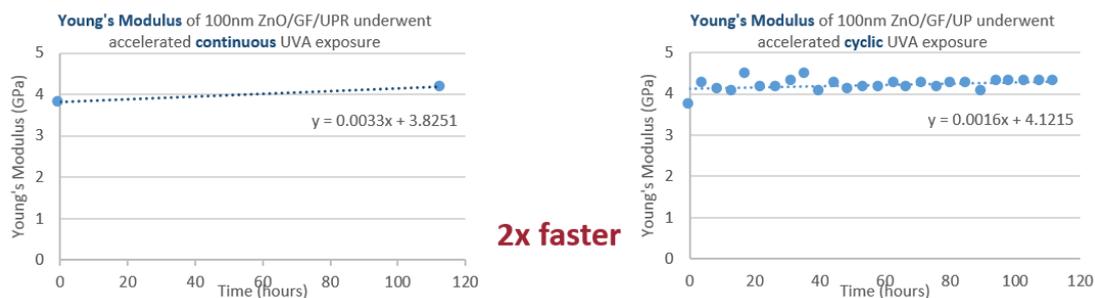
**Figure 1.** Degradation rate of 6 wt.% 100nm undoped ZnO/GFRPs underwent continuous and cyclic UVA exposure

Hardness of Pure E-SMP and ZnO/E-SMPs before and after UVA Degradation
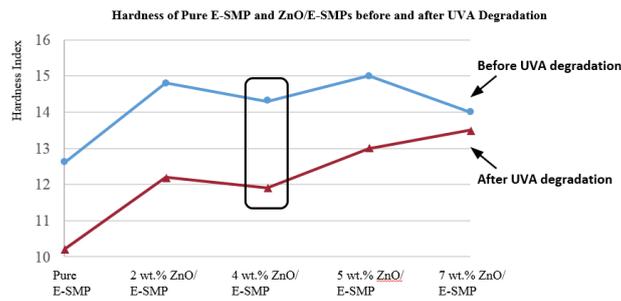
Figure 2. Hardness of 100nm undoped ZnO/epoxy-based SMPs before and after UVA exposure

Hardness of Pure S-SMP and ZnO/S-SMPs before and after UVA Degradation
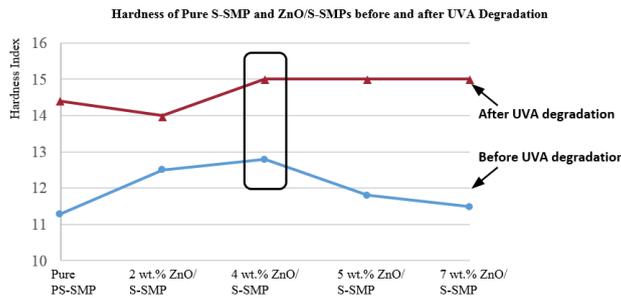
**Figure 3.** Hardness of 100nm undoped ZnO/styrene-based SMP before and after UVA exposure

UV Absorbability of Pure E-SMP before and after UVA Degradation
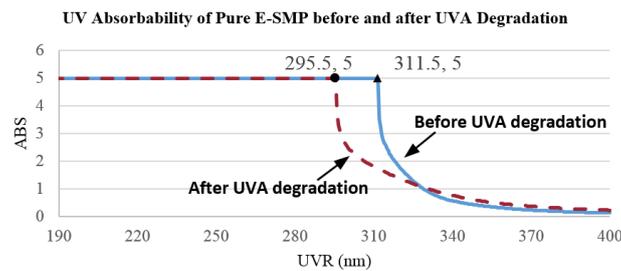
Figure 4. Decrease in UVR absorbability of pure epoxy-based SMP after UVA exposure

UV Absorbability of Pure S-SMP before nad after UVA Degradation
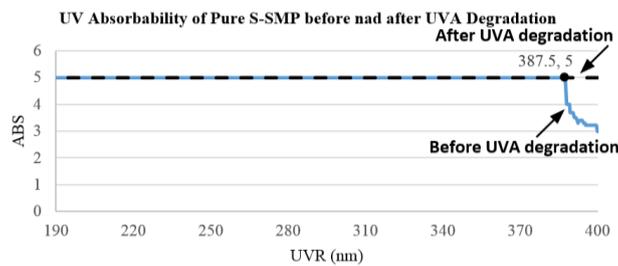
Figure 5. Increase in UVR absorbability of pure styrene-based SMP after UVA exposure
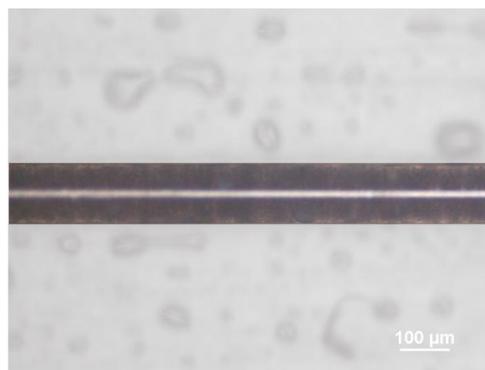
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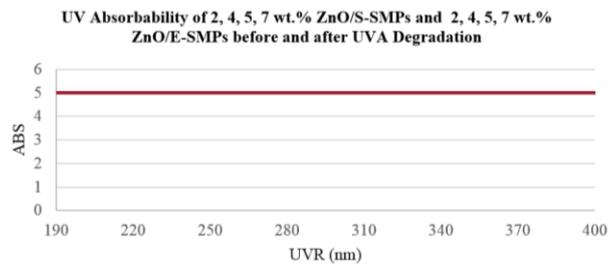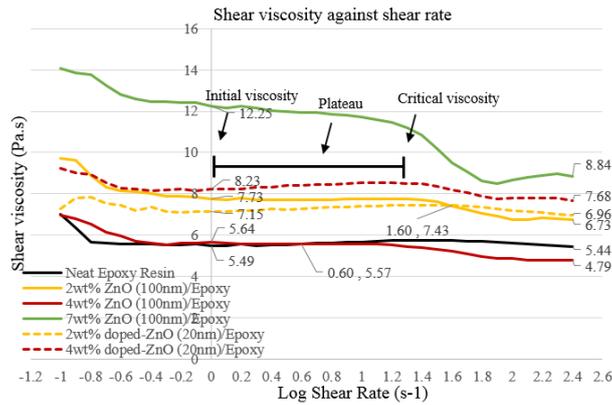
Figure 6. A whole range of UVR absorbability of 100nm undoped ZnO/SMPs
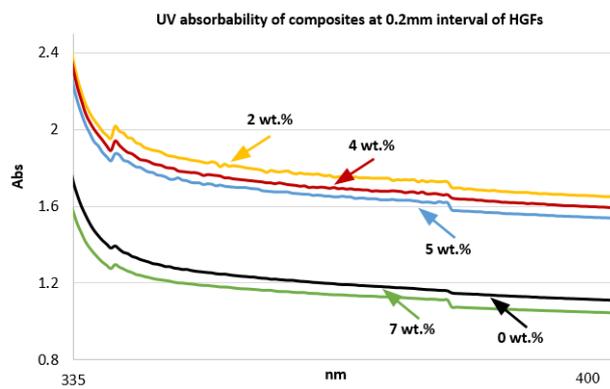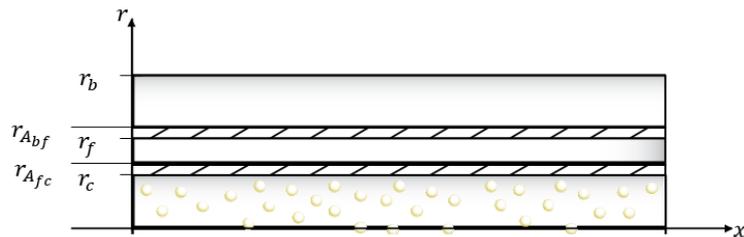

Figure 7. 100nm undoped ZnO/epoxy filled HGF composites

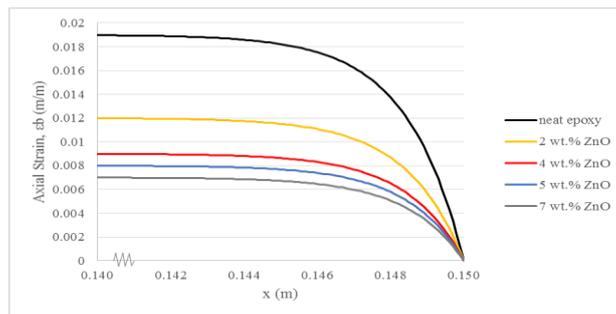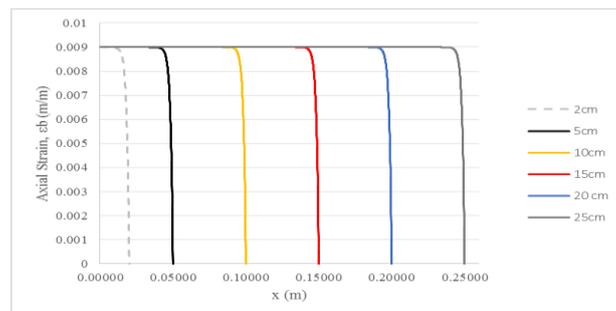**Figure 8.** Even and dense dispersion of 4 wt.% 100nm undoped ZnO in HGF

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**Figure 9.** Rhoelogy properties of 100nm undoped and 20nm doped ZnO/epoxy in HGF

Figure 10. A quarter of ZnO/epoxy/HGF composite system
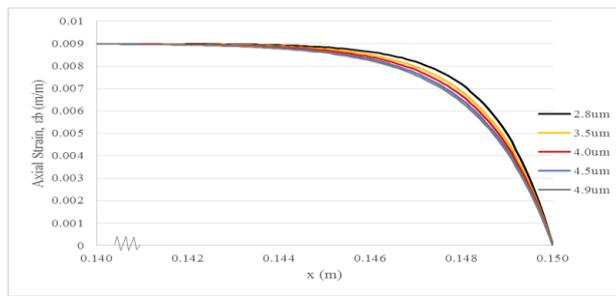

Figure 11. Strain deformation of epoxy base under fibre pull-out with different contents of ZnO nanoparticles in core

Figure 12. Strain deformation of epoxy base under fibre pull-out with different length of HGF

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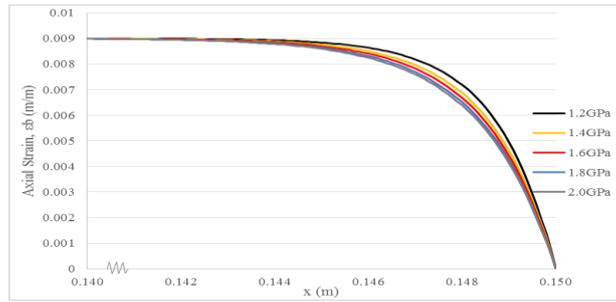
Figure 13. Strain deformation of epoxy base under fibre pull-out with different shear strength of adhesive layers

Figure 14. Strain deformation of epoxy base under fibre pull-out with different thickness of adhesive layers

2.2. Equations

A theoretical model (Eq. 1) is developed to examine the stress transfer ability of the newly-configured layer system containing physical dimensions and mechanical properties of different conponents:

$$\varepsilon_b(x) = \varepsilon_c \left[1 - \frac{v\sinh(ux) - u\sinh(vx)}{v\sinh(uL_f) - u\sinh(vL_f)} \right] \tag{1}$$

and

$$v = \sqrt{G_A \left[\left[-\frac{1}{①} + \frac{1}{②} + \frac{1}{③} + \frac{1}{④} \right] \pm \sqrt{\left[\frac{1}{①} - \frac{1}{②} - \frac{1}{③} - \frac{1}{④} \right]^2 + 4 \left[\frac{1}{①②} - \frac{1}{②④} + \frac{1}{①③} \right]} \right]}$$

$$u = \sqrt{G_A \left[\left[\frac{1}{①} - \frac{1}{②} - \frac{1}{③} - \frac{1}{④} \right] \pm \sqrt{\left[-\frac{1}{①} + \frac{1}{②} + \frac{1}{③} + \frac{1}{④} \right]^2 + 4 \left[\frac{1}{①②} - \frac{1}{②④} + \frac{1}{①③} \right]} \right]}$$

$$① = E_b (r_b - r_{A_{bf}})^2 \ln\left(\frac{r_{A_{bf}}}{r_f}\right)$$

$$② = E_c r_c^2 \ln\left(\frac{r_{A_{fc}}}{r_c}\right)$$

$$③ = E_f (r_f - r_{A_{fc}})^2 \ln\left(\frac{r_{A_{fc}}}{r_c}\right)$$

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$$\text{④} = E_f(r_f - r_{A_{fc}})^2 \ln\left(\frac{r_{A_{bf}}}{r_f}\right)$$

where r_b, $r_{A_{bf}}$, r_f, $r_{A_{fc}}$ and r_c represents the outer radii of epoxy base (*b*), adhesive layer (A_{bf}), HGF (*f*), adhesive layer (A_{fc}) and ZnO/epoxy core (*c*) counted from the centre of ZnO/epoxy core ($r = 0$); E_b, E_f and E_c represent the Young's moduli of epoxy base, HGF and ZnO/epoxy core. G_A represents the same shear moduli of adhesive layers.

3. Conclusions

Several findings from the present study on the effects of UVR in polymer-based composites are summarized as follows:

- The top layer of ZnO/epoxy/HGF is introduced for protecting the core FRPs from UVR degradation, maintaining the surface strength and preventing particles from dissolution and wearing out.

- 4 wt.% 100nm undoped ZnO/epoxy/HGF composite achieve the best UVR absorption among the tested samples. Its better UVR absorption is an account of the good rheology properties and the even particle dispersion inside HGF. A good stress transfer ability of this composite system is confirmed by the developed theoretical model.

- 4 wt.% 100nm undoped ZnO/EP-SMP and S-SMPs and 6 wt.% 100nm undoped ZnO/GF/UP and EP composites achieve a full UVR absorption.
- Silane-doped ZnO is found to be ineffective for UVR absorption.
- UVR absorbability of polymer-based materials are dependent on the boning strength and the molecular chain density.
- Degradation rate given by the change of the Young's Modulus of 6 wt.% 100nm undoped ZnO/GF/UP composite underwent continuous UVA exposure is 2x faster than cyclic exposure.
- A question is raised on the validation of accelerated UVR exposure test to simulate natural UVR exposure.

References

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