



Synergistic environmental degradation of glass reinforced polymer composites



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ARTICLE INFO

Article history:

Received 7 June 2016

Accepted 27 June 2016

Available online 28 June 2016

Keywords:

Glass reinforced polymers

Environmental degradation

Synergistic effects

Ultraviolet degradation

Condensation degradation

ABSTRACT

Synergistic effects involved in the environmental degradation of Glass Reinforced Polymer (GRP) composites were examined in this research. Six GRPs based on E-glass and ECR-glass fibers with four different polymer resins were exposed either individually or in combination to ultraviolet (UV) radiation, water condensation and elevated temperature for approximately 1000 h. The composites were monitored for weight changes as a function of time and their surfaces were examined after the tests using optical and scanning electron microscopes. A new model of synergistic aging of polymers under UV and water condensation was also proposed. It has been shown that the selected aging conditions created noticeable synergistic effects causing extensive erosion of the polymer matrices of the tested composites which appeared to be much stronger under the combined actions than under individual exposures. The differences in the aging rates under the individual and combined situations were adequately explained using the newly proposed model. It is suggested that the surface erosion of polymer matrices of the GRPs by combined UV and water condensation creates the most effective condition for small polymer particles formed by UV to be subsequently removed by water condensation exposing fresh still undamaged surfaces to further UV degradation. It has also been shown that depending on the size of the particles different particle removal mechanisms occur on polymer surfaces eroded by a cyclic exposure to UV and water condensation.

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1. Introduction

Numerous studies have focused on the environmental degradations of Polymer Matrix Composites (PMCs) in general, and more specifically, aging of Glass Reinforced Polymer (GRP) composites caused by a large variety of aggressive environments. Some of the most recent studies can be found in Refs. [1–6]. Very few of them, however, have dealt with the synergistic effects of aging of polymers and GRPs under combinations of several aging conditions [6,7,8]. Since this work is concerned with synergistic aging of a group of commercially available GRPs under combined UV radiation, moisture, temperature and time, an emphasis is made here to evaluate the research progress made so far in this very important area of polymer and polymer based composite science.

The UV components of sunlight which reach the ground are in the range of 280–400 nm [28]. The energy of ground reaching UV

photons is comparable to the dissociation energies of polymer covalent bonds [9–11] resulting in a loss of surface gloss, surface discoloration, chalking, flaking of surface resin, pitting, micro-cracking, and a severe loss of resin [7–13] in GRPs. The damaging effect of water or moisture on polymer composites, on the other hand, is not as harsh as degradation just by UV radiation even at elevated temperatures [7]. However, moisture diffusion into polymer matrix/fiber interfaces can damage the interfaces by micro-cracking [14,15] especially at elevated temperatures. In addition, hydrolysis of chemical bonds may lead to permanent chemical degradation [1,15,16] and moisture induced swelling [1,14,17] of polymers and their composites.

The combined action of both UV and water on polymers and PMCs as a function of time and temperature could be even more severe than the individual effects. Therefore, this topic has been addressed here both experimentally and numerically. It should be stated that the objective of this work was not to rank a group of GRP composites for their resistance to the above aging conditions, but to investigate the fundamental aspects of the combined UV/water aging processes applicable to any GRP, and more generally, to any

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PMC system.

2. Experimental procedures

2.1. Tested composites and specimen preparation

The composites tested in this research are listed in Table 1. The exact chemical compositions of the composites were not released for the purpose of this study. Also, the matrix of composite F is proprietary information.

Two groups of unidirectional GRP composites were investigated. In the first group, three composites (A, B and C) with E-glass, ECR-1 glass and ECR-2 glass fibers in a vinyl ester epoxy blend matrix were tested to evaluate the fiber effect on composites' degradation. In the second group, one type of fiber, ECR-2 glass, was considered with four different polymers, namely polyester, vinyl ester, epoxy and a proprietary resin to determine the matrix effect on the degradation processes in composites C, D, E and F. The fibers came from three different glass manufacturers and the composites were supplied by MacLean Power Systems.

1.3 m long, 6 mm thick and 50 mm wide composite plates were made by pultrusion by an outside manufacturer. The weight fractions of fibers in the six systems were very similar (Table 1). The composites were dry cut before testing into 80 mm long specimens with special care to ensure minimum damage during cutting. The cut edges of the samples were sealed with a thin layer of a room temperature vulcanization silicone. Subsequently, the specimens were heat-treated for 72 h in an oven at 80 °C. The other as supplied surfaces of the samples were smooth and glossy before the tests.

2.2. Environmental testing and analysis

A Q-LABQUV/SPRAY/RP chamber was used for individual and combined UV radiation and water condensation aging tests. The UV radiation tests were carried out for 1000 h with the UV wavelength ranging from 315 to 400 nm at 80 °C. An irradiance level of 1.50 W/m² at 340 nm was chosen to more than double the maximum irradiance of natural sunlight at noon. The test temperature was lower than the glass transition temperatures, T_g, of the polymer matrices of the composites, which were higher than 120 °C. The relative humidity (RH) was 3 ± 2% and was recorded by a relative humidity meter placed inside the chamber.

In the water condensation tests the specimens were continuously exposed to deionized (DI) water vapor condensation at 60 °C for 1000 h with 92 ± 2% RH. Water condensation was formed by heating deionized water to vapor on a hot panel inside the chamber. In the cyclic UV radiation and water condensation tests, the composites were exposed to alternating cycles consisting of 16 h of UV at 80 °C followed by 8 h of water condensation at 60 °C for 1000 h. The relative humidities were 33 ± 2% and 92 ± 2%, respectively.

For weight measurements the specimens were removed every 96 h from the chamber for about 60 min and weighed with an Ohaus Voyager Electronic Balance (precision 0.01 mg). The

specimens were then randomly repositioned in the chamber to ensure uniform exposure on all surfaces. The percent weight changes as a function of time were calculated using Eq (2.1):

$$\%weight\ change = \frac{W_f - W_i}{W_i} \times 100 \quad (2.1)$$

where W_f and W_i are the final and initial dry weights of the samples at room temperature.

Optical and scanning electron microscopes (SEM, JSM 500 LV) were used to evaluate the surface morphology of the specimens after their exposure. All specimens were prepared and mounted using conventional procedures for SEM observations. Most of the work on the surface deterioration in the composite under the above testing conditions has been reported elsewhere [18].

3. Aging results and discussions

3.1. Surface erosion

Surface characteristics of all tested composite specimens after their exposures to UV, water condensation and combined UV/condensation were examined optically and by the SEM. Despite significant differences in their original surface properties such as the amounts of exposed glass fibers, fiber distributions, fiber alignment, fiber diameters, etc. [19], all composites, including A, responded in quite similar fashions to all three test environments with the exception of composite D. Therefore, A was picked as an example to illustrate the aging effects on the composites (Fig. 1A). The polyester composite (D) had apparently UV blockers applied to its resin which resulted in less surface damage by UV (Fig. 1B). D also had more exposed fibers on the surface (approximately 13% in comparison with A (2.8%). In some cases the exposed fiber areas were as large as 50% (composite E).

Surface damage characteristics under individual UV, water condensation and combined UV and water condensation on Vinyl ester Epoxy ECR-Glass 1 – Composite A are shown in Fig. 2 (UV only), Fig. 3 (condensation) and Fig. 4 (UV/condensation combination). Distinct differences in surface erosion can be observed on the surfaces subjected to the three different aging conditions.

Fig. 2 shows severe matrix degradation with numerous small particles ranging from a micron or smaller to about 20 μm formed on the surface by chalking. This phenomenon was caused by the polymer matrix becoming excessively brittle due to an increased crosslinking or the formation of microcracking due to chain scission resulting from photo-oxidation reactions induced by UV radiation [20]. The removed layer of the matrix was more than 20 μm deep. The fibers and the fiber/matrix interfaces in all composites were unaffected by UV. Previous research reported that degradation on polymers surfaces by UV is a time dependent effect where the photochemical reactions are restricted to the surface of the polymers within a several micron thick layer [21].

The micrographs presented in Fig. 3 indicate that the matrix and the interfaces of the composite were degraded by water condensation and the amount of degradation was not uniform across the surface. Overall the amount of damage by water for all composites was much less severe than the damage illustrated in Fig. 2 for the UV exposure.

Cyclic exposure to both UV radiation and condensation resulted in severe degradation that was very different from the other two exposures. The damage consisted of extensive matrix erosion and debonding. As shown in Fig. 4, the external polymer layer on the specimen surface was completely removed and the underlying glass fibers were exposed. Most importantly, all samples were almost entirely free from any particles larger than a few microns in

Table 1
Tested GRPs.

Label	Matrix	Glass fiber	Weight fraction (%)
A	Vinyl ester epoxy	ECR-glass 1	75
B	Vinyl ester epoxy	E-glass	75
C	Vinyl ester epoxy	ECR-glass 2	80
D	Polyester	ECR-glass 2	80
E	Epoxy	ECR-glass 2	80
F	Proprietary	ECR-glass 2	80

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