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Dissolving Cylinder Zero-Order Kinetic Model for Predicting Hygrothermal Aging of Glass Fiber Bundles and Fiber-Reinforced Composites

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Abstract

Glass fibers and fiber-reinforced composites degrade when exposed to water. Understanding the dissolution behaviour of glass in fiber-reinforced composites is necessary to predict the changes in physical and mechanical properties of composites. The degradation of glass fibers follows two distinct kinetic regions: short-term non-steady-state and long-term steady-state degradation. In the short-term, the degradation is complex and involves such processes as ion exchange, gel formation and dissolution. When long-term steady-state is reached, the dissolution becomes dominant and the degradation follows zero-order reaction kinetics. The purpose of this study is to present an analytical model that describes kinetics of dissolution of R-glass in fiber bundles and in fiber-reinforced composites. Effects of sizing, availability of water and accumulation of degradation products are discussed. The model is able to predict mass loss during hygrothermal aging of glass fiber bundles and fiber-reinforced composites.

2. Introduction

Glass fibers are hydrophilic and are susceptible to a relatively slow degradation when exposed to water environments [1]. Much of the confusion related to the modelling of degradation of glass fibers is due to the fact that dissolution is not the only process involved in degradation,

thus making the whole process a combination of competing subprocesses such as ion exchange, gel formation and dissolution. This is, however, causing issues mostly on the short-term [2]. In the long-term, the degradation process is governed by dissolution and follows zero-order reaction kinetics [2,3]. Si contribution to the total mass loss of studied R-glass fibers is the largest (56.1 % by mass) and seems to govern the dissolution process [3]. The dissolution of glass fibers inside composites is slowed down compared to unprotected fiber bundles [4]. This phenomenon can be explained due to effects of availability of water and accumulation of degradation products. These aspects are addressed in the analytical model.

3. Experimental

Boron-free and fluorine-free high strength, high modulus 3B HiPer-tex W2020 R-glass fiber bundles and mats were used. Composite laminates were prepared via vacuum assisted resin transfer molding (VARTM) using Hexion Epikote RIMR135 epoxy resin and Hexion Epikure RIMH137 amine curing agent in proportion 100:30 by weight. Sizeless and sized glass fiber bundles and composite plates were used for glass dissolution measurements. Composite plates had dimensions of 20x20x1 mm with fibers oriented parallel (C1 plates) and normal (C3 plates) to the large face of the plate, respectively (as shown in Figure 1).

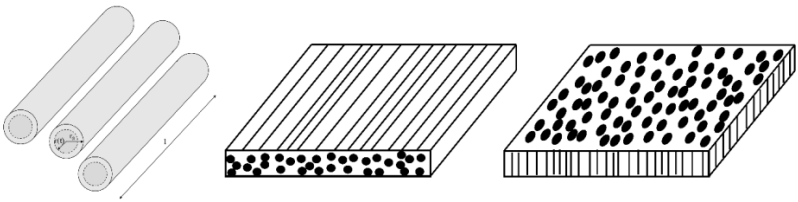

Figure 1. Sample configurations from left to right: fiber bundles, composite plates C1 and C3.

Samples for dissolution study were placed in inert closed vessels filled with distilled water that were kept in a water bath with a PID-controlled temperature of 60 ± 1 °C. Water from the vessels was analyzed in time via high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) providing glass dissolution kinetics.

4. Results and discussion

The model presented here is a general case of a model for glass fiber bundles described in another work [3]. The rate of the dissolution is dependent on the zero-order reaction kinetic constant (K_0), the glass surface area exposed to water (S), presence of sizing (ξ_{sizing}), the availability of water (C_{H_2O}) and the order of the reaction (n_{order}). In addition, as the aging proceeds, degradation products are accumulated in the composites and slow down the rate of the reaction. Since the long-term reaction is governed by Si dissolution [3], the silica hydrolysis products are what causes the deceleration of glass dissolution inside the composites. In the model, the accumulation term is accounted for as a driving force term, that shows that rate of the mass loss is proportional to the difference between saturation ($C_{SiO_2}^{eq}$) and current concentration (C_{SiO_2}) of degradation products in the composite and the order (m_{order}). The global model (general case) can then be mathematically expressed as the following equation:

$$\frac{\partial m}{\partial t} = K_0 \xi_{sizing} S C_{H_2O}^{n_{order}} \left(C_{SiO_2}^{eq} - C_{SiO_2} \right)^{m_{order}} = K_0^* S$$

where m is a total cumulative mass dissolved after time t; K_0^* is an apparent reaction kinetic constant that can be obtained from regression of experimental data. While K_0 is a material property, K_0^* incorporates effects of sizing, water availability and degradation product accumulation.

For fiber bundles in large volume of water, conditions of infinite availability of water ensue, the rate of reaction becomes independent of reactant (water) concentration, and the reaction order n_{order} becomes 0. For fiber bundles in large water volumes there is no accumulation term as well, so that apparent reaction kinetic constant K_0^* and the material property K_0 are equivalent. For fibers, in infinite water availability conditions, the surface reaction can be well-described with zero-order kinetics [5], but the decrease in fiber radius and thus surface area as reaction proceeds should be accounted for [3]:

$$\frac{\partial m}{\partial t} = K_0 S = K^*_{0_{sizeless\ fibers}} S$$

For sized fibers, effect of sizing (ξ_{sizing}) should also be accounted for:

$$\frac{\partial m}{\partial t} = K_0 \xi_{sizing} S = K^*_{0_{sized\ fibers}} S$$

Model parameters obtained from experimental long-term dissolution kinetics data for Si loss from sizeless and sized glass fiber bundles and composite plates are reported in Table 1. The goodness of fit with experimental data is represented by determination coefficients R^2.

Table 1. Long-term dissolution of R-glass fiber bundles and reinforced composite plates.

	K_0^* (g Si/m^2·s)	**R^2**
Sizeless Fiber Bundle	$2.30 \cdot 10^{-9}$	0.9576
Sized Fiber Bundle	$3.80 \cdot 10^{-10}$	0.9781

Composite Plate C1	$1.32 \cdot 10^{-10}$	0.9953
Composite Plate C3	$2.40 \cdot 10^{-10}$	0.9923

The long-term dissolution of glass from composite plates C1 and C3 is slowed down by 65.26% and 36.84%, respectively, compared to sized fiber bundles. The effect of sizing on glass dissolution was found to be almost an order of magnitude with a value of ξ_{sizing} being equal to 0.165. Measurements with different sample configurations allowed to decouple water availability and accumulation terms. By using a combination of short interface (sizing) highways (1 mm) in composite C3 plates, where accumulation was assumed to be non-present, and composite C1 plates with fairly long interface highways (20 mm), it was possible to obtain water availability and accumulation terms. The water availability is governed by the water saturation levels of epoxy matrix. For the plate C3 with no accumulation term, the order of reaction n_{order} can be obtained as follows:

$$n_{order} = \frac{\log \frac{K^*_{0_{composite}}}{K_0 \xi_{sizing}}}{\log C_{H_2O}}$$

On a first approximation, assuming that water availability term is independent of fiber orientation and is equivalent for cases of C1 and C3, it is possible to estimate the accumulation term $\left(C^{eq}_{SiO_2} - C_{SiO_2}\right)^{m_{order}}$ as follows:

$$\left(C^{eq}_{SiO_2} - C_{SiO_2}\right)^{m_{order}} = \frac{K^*_{0_{composite}}}{K_0 \xi_{sizing} C^{n_{order}}_{H_2O}}$$

5. Conclusions

Analytical model for prediction of long-term dissolution of glass from both glass fiber bundles and fiber-reinforced composites was presented and explained. The model describes mass loss kinetics during hygrothermal aging. The sizing slowed down glass dissolution of fiber bundles by almost an order of magnitude. Compared to dissolution of sized fiber bundles, the long-term dissolution of glass from composites was slowed down by 36.84% and 65.26% depending on fiber orientation. Slower dissolution from composites compared to unprotected unsized glass was explained with the effect of sizing, limited water availability via protecting polymeric matrix and due to silica degradation product accumulation inside the composite.

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