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Damage detection and self-repair in hollow glass fiber fabric-reinforced epoxy composites via fiber filling

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ABSTRACT

Hollow glass fiber reinforced epoxy matrix composites were produced to study whether the damage development can be followed and the self-repair can triggered by filling the fibers with suitable additives. Composite plates were manufactured by the hand layup and vacuum assisted resin transfer molding techniques. To detect subcritical transverse impact damage, hollow fibers were filled with an ultraviolet fluorescent dye, whereas for self-repair, they were filled with a polyester resin along with the corresponding accelerator. The healing process was induced at different temperatures and continued for different durations. It was demonstrated that the targeted damage detection and self-repair can be achieved using thin (10–13 μm outer diameter) reinforcing hollow fibers. The self-repairing ability was demonstrated in three point bending tests and the healing was confirmed by inspection with scanning electron microscopy.

1. Introduction

Microcracks in fiber reinforced composites, which are initiated mostly under fatigue and impact conditions, should be repaired before fast crack propagation and catastrophic failure occur. The microscopic damage may be diminished by self-healing, provided that a type of repair liquid flows into the cracks and fills them properly. The latter means that the repair liquid adheres to the crack flanks and provides suitable cohesive strength at the same time. The idea of self-reparation comes from nature. As trees bring resin to their injuries, or as mammals heal their skin injuries by bleeding, the composites may also store some healing liquid. Recommendations for the storage of healing agents in composites have already been made [1]. One possible element for storing the liquid is the hollow fiber, embedded into the matrix, which can transport the healing liquid wherever it is necessary. The healing liquid flows into the crack and restores the connection between the broken parts [2]. Self-repair and damage assessment are of interest for concrete parts [3,4], polymers [5,6] and related composites, as well [7–10]. Hollow fibers may also contain different "indicator" liquids, which can help us to detect the damage development. Storing the healing agent in hollow fibers in composites is more advantageous than storing it in microcapsules [11–13], or in vascular networks [14–16], because they can store larger amounts than microcapsules and still provide efficient reinforcement.

Motuku et al. [17] used different solid and hollow tubes in composites. Their basic concept for self-repair was to use hollow fibers filled with suitable agents alongside solid reinforcing fibers. They examined the alteration of the energy absorbing capability of plates after impact-induced damage and after migration of the healing agent to the damaged areas. Vinylester matrix-based self-repairing composite (SRC) plates were their model materials. It was demonstrated by optical microscopy that the hollow fibers do not alter the failure mode compared to that of conventional composites. The SRCs with hollow fibers were damaged by low velocity impact in the same manner as conventional composites.

Trask et al. [18] used hollow glass fibers (HGF) for the storage of the repairing agent. The outer diameter of the fibers was 60 ± 3 μm and the degree of hollowness was 55% (the ratio of the outer to the inner diameter). HGFs were embedded into carbon fiber-reinforced composites, and the hollow fibers were filled with a healing agent to study the self-repairing function. The matrix of the composite and the healing liquid were both two-component epoxy resins. Inside the laminate, the HGFs were placed 70 and 200 μm apart. The fracture of the specimens was executed with a steel ring pushed onto the specimens with 1700 and 2000 N loads. The bending strengths of the reference specimens (without HGF),

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undamaged SRC, the damaged and healed SRC were measured. The healing fibers placed at 70 μm deteriorated the bending strength of the undamaged laminates markedly (8%), but the results after healing were better because of the greater amount of healing material (1700 N: 91%, 2000 N: 89% residual strength) than in the other sample with the fibers placed 200 μm apart (1700 N: 90%, 2000 N: 80%). Contrarily, the bending strength reduction caused by the hollow fibers was lower in the case of 200 μm placement (2%).

Pang and Bond [7] filled the hollow fibers with resin mixed with ultraviolet (UV) fluorescent dye so the self-repairing function could be triggered by an UV lamp. Thus, the position of the cracks and the healing process caused by the flow of the resin flow into the cracks could be monitored. Laminates were prepared with outer layers of 0°/90° lay-up using conventional E-glass fabrics and with inner layers using borosilicate HGF unidirectional fabrics. The outer diameter of the HGFs was 60 μm and the hollowness was 50%. The 0° directional HGFs were filled with the resin component and the 90° directional HGFs were filled with the hardener mixed with a UV fluorescent dye. Specimens were fractured after different periods (0, 3, 6 and 9 weeks) to examine the effect of time on the healing ability of the curing agent. A 24 h curing period was given to the composite for healing via resin crosslinking. Four point bending tests were performed on the specimens. The bending strength of the damaged, unfilled specimens was 25% lower than that of the undamaged, unfilled ones. The first self-repairing tests were performed immediately after filling the HGFs of the cured composite. The bending strength of these specimens was 93% of that of the unfilled, undamaged ones. With elapsed time the healing ability was reduced, and after a 9 week period it ceased. Obviously, the healing resin was affected by the storage conditions and the environment, and thus it could no longer fulfill its role as a healing agent.

Regarding the previous studies, it can be concluded that a self-healing function is possible with hollow fiber reinforcement, but the required diameter of the fibers is well above the ideal diameter that does not deteriorates the mechanical properties of the composites. The aim of our research was to develop a damage-detecting and a self-repairing composite which is reinforced with thin hollow fibers. Thin hollow fibers should ensure a reinforcing function. For the healing agent, a polyester resin was selected because it is less sensitive to the mixing ratio of the components than the epoxy resin used in the previous studies [7,18–21]. A further aim of our study was to define an impact examination method that can be easily reproduced, which allows us to determine the healing ratio adequately. The effects of the repair periods and the repair environments on the healing rate were also examined.

2. Materials

The HGF fabric was obtained from R&G Faserverbundwerkstoffe GmbH (Waldenbuch, Germany). The fibers are made of H-glass, using a patented mixture of an alkali free aluminum–borosilicate by a proprietary manufacturing method. The nominal outer diameter of the fibers was 10–12 μm, while the inner diameter was 5–6 μm. The weight of the fabric is 160 g/m^2, and the structure was a 0°/90° atlas weave.

For the matrices of the composites manufactured by vacuum assisted resin transfer molding (VARTM) and hand layup (HLU), respectively ipox MS90 (Ipox, Budapest, Hungary) and Ciba 5082–5083 (Ciba, Basel, Switzerland) resin systems were selected. Eporezit AH12 resin was chosen as epoxy carrier for the indicator liquid. It was "colored" by the UV fluorescent indicator, viz. Keystone Rhodamine B Base (Keystone, Chicago, USA). For damage detection in the composites, their matrices were painted with Eporezit SZPM white dye. This was incorporated at 5 wt% in order to ensure a better resolution for damage inspection. The coloring is important because without it, the painted indicator liquid can be observed through the glass fibers and the initially transparent matrix. "Coloring" of the matrix in this way is a straightforward method to support the detection of the indicator liquid, which is flowing onto the surface of the damaged composite. The healing agent was Polimal 1058 (Polimal, Poland) injectable polyester resin system.

3. Technologies

3.1. Manufacturing of the composite plates

During the manufacture of the HGF reinforced composites it was important to avoid matrix resin flow inside the fibers. In case of the HLU, the laminate was put under weights and placed on a glass plate to guarantee an equal distribution of the resin within the composite. Composite plates were cured for 24 h at room temperature (23°), followed by an 80 °C heat treatment in an oven for 8 h.

3.2. Filling of the hollow glass fiber reinforced composites with liquids

It is very important when filling the hollow fiber reinforced plates that the ends of the fibers should not be clogged. After cutting the specimens, they were ultrasonically cleaned and were conditioned in a Heraeus UT6 (Hanau, Germany) air drying oven for 10 h at 60 °C. The filling layout is shown in Fig. 1.

After drying, one edge of the specimens was placed into a vacuum bag (1) with a flow medium net (2) on both sides. Therefore, the hollow fibers remained accessible for the resin. The other end of the specimens was placed into the filling liquid (3). Recall that this was either the polyester healing resin or the colored ("painted") epoxy resin. To become self-repairing the hollow fiber reinforced composites were filled with a catalyzed unsaturated polyester resin and with its initiator (methyl ethyl ketone peroxide) dissolved in dimethyl phthalate (trade name: Butanox M50, Amersfoort, Netherlands, Akzo Nobel Company). To reach the adequate mixing ratio (resin/initiator, 100:5) only a smaller portion of the fibers had to be filled with the initiator (maximum 10%). For this purpose a special specimen was required. Therefore, to control the positions of the peroxide-containing fibers the composite plate was notched with a ribbon-saw. Where the composite was not notched, the fiber remained intact and could be filled with peroxide. On the side, where the filling with peroxide was executed, the composite plate was not notched (4). The preparation of the specimens begun with saw-cutting yielding the "notches", so unnotched sections remained (4). The width of each unnotched section was 3 mm and the distance between them was 22 mm. Prior to filling the fibers all edges of the plates were cleaned with an ultrasonic cleaner in acetone for 30 min. Thereafter they were dried for 12 h at 60 °C. The first step of the filling process was to fill the specimens with peroxide. The unnotched sections (4) were immersed into the liquid, and the other ends of the specimens were placed under suction by a vacuum bag. After filling the vertical longer fibers with peroxide, they were isolated by plasticine. In the second step, the polyester resin was introduced into the shorter fibers prepared by the saw cutting from the upper side of the specimens, so that gravity also supported the filling. When the filling was finished, the vacuum bags were removed from both sides of the specimens. In this way, all of the vertical fibers were filled–the longer ones with peroxide and the shorter ones with the healing polyester resin. Afterwards, the initial horizontal fibers in the fabric should be filled with the healing