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Local repair procedure for carbon-fiber-reinforced plastics by refilling with a thermoset matrix

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ABSTRACT: Textile-reinforced composites have given rise to an increasingly important key technology for lightweight construction in aerospace, automotive, civil engineering, and many other industries. Because there exists no suitable repair procedure for carbon-fiber-reinforced plastics (CFRPs), damaged parts have to be replaced completely; this is extremely disadvantageous both ecologically and economically. With fiber-reinforced composites used being more and more often, fast and efficient methods for the local repair of damaged CFRPs are essential. In this article, a novel repair procedure for CFRP is presented. The thermal activation by IR radiation of oxide semiconductors was used to locally degrade the thermoset matrix of the damaged CFRP through the maintenance of its structural stability and properties. The matrix-free textile structure was then refilled with a thermoset epoxy matrix. Carbon fibers from the treated area were characterized with scanning electron microscopy, IR spectroscopy, thermogravimetric analysis, and subsequently, tensile strength for single fibers to verify the effectiveness of the procedure. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42964.

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INTRODUCTION

The growing demand of efficiency in various fields of mechanical engineering has led to an increased research focus on lightweight constructions based on fiber-reinforced plastics. These composites feature outstanding mechanical properties, such as a high tensile strength, high stiffness, good fatigue resistance, resistance to corrosion, and low thermal expansion. Hence, they are used in various applications in aerospace, automotive, marine, wind energy, and sporting industries.[1–3]

Typically, two or more distinct materials are combined for the preparation of composites, for example, a high-tensile fiber and a plastic matrix. Common fibers applied in composites are made of glass, carbon, aramid, basalt, and ceramic.[4] Thermoplastics or thermosets are used as matrix materials.[5]

The repair of partially damaged fiber-reinforced plastics is challenging, in particular when nonmelting thermosetting polymers, such as epoxy and phenolic resins, are used as the matrix material. Currently damaged parts are often replaced completely, regardless of the extent of the defect. Damages generally occur as traverse and longitudinal fractures, debonding, and fiber breakages (Figure 1); this causes a significant decrease in the functionality.[6] Hence, repair methods focusing on the full recovery of the mechanical functionality of damaged composites are an increasing focal point of research.[7,8] Furthermore, economic issues and ecological aspects also need to be considered during the introduction of an innovative repair concept.[9]

A currently applied repair method in the aerospace industry is the so-called scarf method, as this technique results in a smooth surface and long-lasting functionality after the reparation of the composites.[10] In brief, manual grinding is applied to remove the damaged surface. Subsequently, the resulting void is bridged and reinforced, respectively, by a metal sheet or carbon fiber (CF) patch in the load direction.[11,12] Finally, the patch is infiltrated by a resin, where the resulting mechanical properties are strongly influenced by the resin processing properties, such as

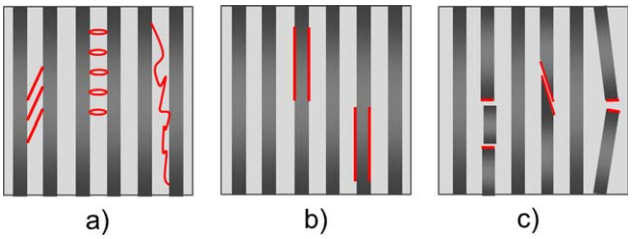

Figure 1. Different types of CFRP defects: (a) matrix cracks, (b) delamination, and (c) fiber breakage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the wettability, viscosity, and air inclusion.[8] This time-consuming procedure is either done manually by trained staff or performed with the help of a special mounting procedure.[13]

The objective of the presented study was the investigation of a universal, facile, and improved local repair method that could be applied to the recovery of the mechanical properties of partially damaged composites. In this method, oxide semiconductors (OSCs) are applied to the surface of a damaged spot of the composite. Subsequently, the spot is heated locally to a temperature ranging from 350 to 500°C through radiation; this initiates a thermal activation of the OSC by means of the generation of electron holes in the valence band. Subsequently, electrons from the matrix polymer occupy the holes, and cationic radicals are formed within the polymer. Through a chain reaction, the polymer is decomposed into smaller molecules and finally into carbon dioxide (CO_2) and water (H_2O).[14,15]

This aforementioned method was adapted here to develop a physicochemical repair procedure with the aim of recovering damaged carbon-fiber-reinforced plastics (CFRPs) through the degradation of the matrix in the damaged spot, as shown in Figure 2. In detail, (1) the damage and its extent were detected, and (2) a suitable OSC was applied to the surface of the damaged area. (3) The thermoset matrix was then locally removed by the thermal activation of the OSC, and (4) this resulted in the exposure of the undamaged reinforcement fiber structure. (5) Finally, the removed matrix material was refilled with a resin.

The success of the repair method was strongly influenced by the type of the chosen OSC. Different compounds were investigated and evaluated; namely, these were cerium(IV) oxide (CeO_2), chromium(III) oxide (Cr_2O_3), nickel(II) oxide (NiO), and titanium dioxide (TiO_2). A first indicator for a usable OSC was the band gap of each OSC and the particle size of the available powders.

In preliminary experiments, the application of Cr_2O_3 showed very promising results. Hence, it was used for further investigations presented here. Furthermore, the applied energy source, such as radiation or hot air, for increasing the local temperature at the damaged spot has to be evaluated. Other possible sources of energy that could be used to activate the OSC are heating rods, flames, lasers, and induction.

EXPERIMENTAL

Analysis

IR measurements were taken with a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, Germany) attached to an attenuated total reflectance unit. For the characterization of the morphology of the CFs, a scanning electron microscope (Zeiss DSM 982 Gemini, Germany) was used. Thermogravimetric analysis (TGA) was done with the help of a TGA

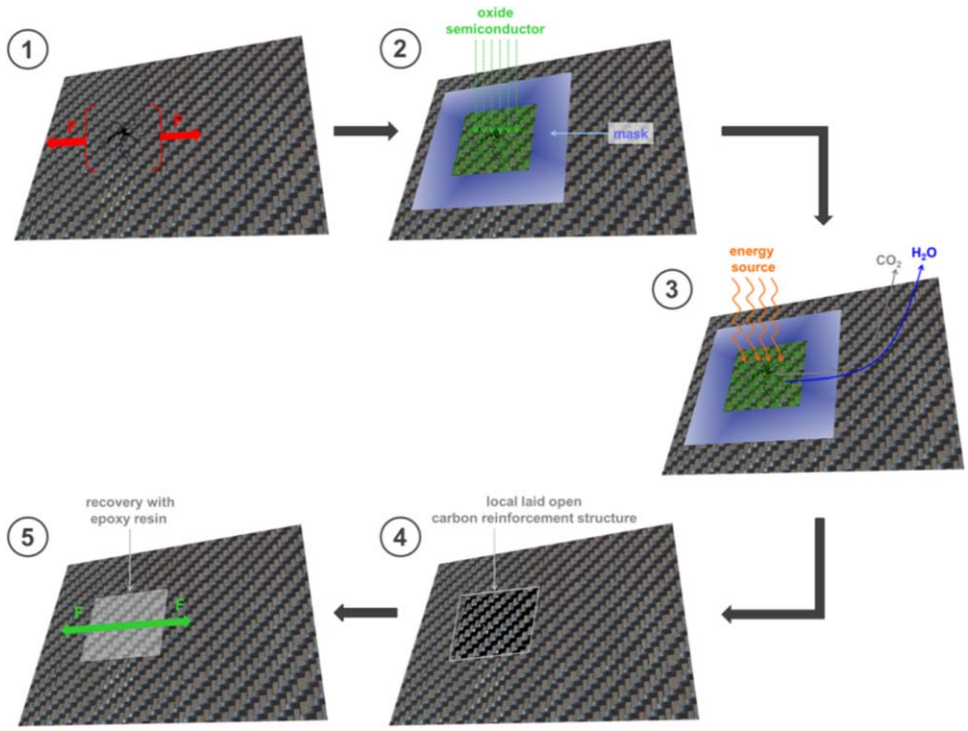

Figure 2. Physicochemical repair procedure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Properties of the Woven Fabric

Weave pattern	Weight (g/m^2)	Density (cm^{-1})		Density (tex)		Thickness (mm) Woven fabric
		Warp	Weft	Warp	Weft	
Twill 2/2	650	4	4	800	800	0,90

Q500 instrument (TA Instruments) and was used for the determination of matrix residues after the degradation procedure and for the calculation of the fiber–volume ratio. Measurements were conducted in a temperature range from 30 to 800°C with synthetic air (80% N_2 and 20% O_2) and various heating rates up to 40 K/min. The testing of the single fibers were carried out with the testing device from Favimat+ and Textecho (Herbert Stein GmbH, Germany) on the basis of DIN EN ISO 5079 ("Determination of Breaking Force and Elongation at Break of Individual Fibers").

Manufacturing of the CFRP Samples

A woven fabric (Sigratex KDK 8004/120) from the SGL Technologie GmbH with the following properties (Table I) was purchased.

Subsequently, two layers of the fabric, the epoxy resin RIM 135, and the hardener RIMH 137 (Hexion Specialty Chemicals B.V.) were used to prepare a CFRP plate with dimensions of 330 x 380 mm^2 and thickness of 2 mm with the RTM method. The infiltrated plates were partly cured at 80°C for 1 h and fully cured at 50°C for 15 h.

Local Matrix Removal and Refilling

The complete experimental setup, which was designed to remove the matrix, is shown in Figure 3. First, a thin layer of Cr_2O_3 powder (Merck Performance Materials, Germany) was applied to the surface of the CFRP plate. A mask (made from glass/ceramic nonwoven fabric) was placed on top of the powder to prevent the adjacent areas from being irradiated. An IR lamp (Heareus Noblelight GmbH, Germany) is placed in a distance of 20–25 mm^2 above the repair area. For matrix removal, voltages of 200 and 380 W was applied for up to 20 min. Afterward, residual Cr_2O_3 was gently removed by a brush and airflow. The exposed reinforcing CFs were then cut from the specimen for following analysis.

For comparison, the area from which the matrix was removed was refilled by an epoxy resin and repaired by the utilization of the Seeman composite resin infusion molding process (SCRIMP) method. Thereafter, the treated CFRP was placed in a vacuum bag and evacuated; this was followed by the infiltration of mixed epoxy and hardener (RIM 135 and RIMH 137). The curing procedure was analogous to CFRP plate preparation.

RESULTS AND DISCUSSION

First, the matrix degradation was optically evaluated. Figure 4 shows the origin CFRP and the CFRP after the local decomposition of the thermoset matrix. The woven carbon reinforcement structure was locally resin-free and laid open by the physicochemical treatment. Despite the high temperatures and resulting local thermal stress, the exposed reinforcing structure remained undamaged and unaffected. The matrix was completely eliminated in an area of 20–50 mm in diameter and up to a thickness of approximately 2 mm. Figure 4(b) shows the resin-free zone with a cross-sectional dimension of 50 mm. The scanning electron microscopy (SEM) images verified the gentle method by revealing clearly intact CFs of the reinforcement structure [Figure 4(c)]. It was also notable that the treated area defined by the mask was very sharply distinguishable from the bordering matrix [Figure 4(d)].

The CF before and after the decomposition of the thermoset matrix (epoxy resin) was also characterized (Figure 5). The two SEM images showed a single CF without any significant differences in appearance between them.

After the optical microscopic investigation of the exposed CFs, the thermal analysis was carried out as a second step. To characterize and understand the reduction of the thermoset matrix, thermogravimetric measurements were done on the used epoxy resin, as shown in Figure 6. All of the TGA measurements were conducted two times without any significant differences.

In general, the oxidation of amine compounds is a very complex process. The TGA curves of the bisphenol A resin hardened by amines without textile reinforcement exhibited various thermal decomposing stages between 300 and 450°C. For the TGA on the used epoxy resin, the measurement was done under synthetic air (80% N_2 and 20% O_2). In various studies, the thermooxidative degradation products of the epoxy resin have been extensively analyzed and described.[16–19]

Adapted from the TGA results, it was obvious that compared to the original CFs, the matrix was completely decomposed by the thermal decomposition exhibited by the underlying woven CFs. Recent research has indicated that thermooxidative degradation of CFs takes place at a temperature of about 600°C.[20] The original CFs were decomposed at a slightly higher temperature of about 730°C compared to that of the CFs recovered from the thermally treated CFRP samples. The temperature difference between the two CF samples was about 15°C; this was within the range of systematic failure of the method. The sizing of the

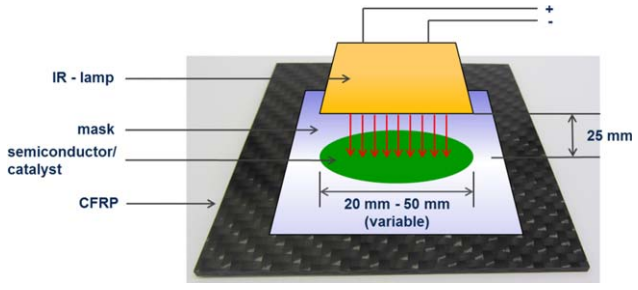

Figure 3. Experimental setup for the local removal of the matrix from the CFRP samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

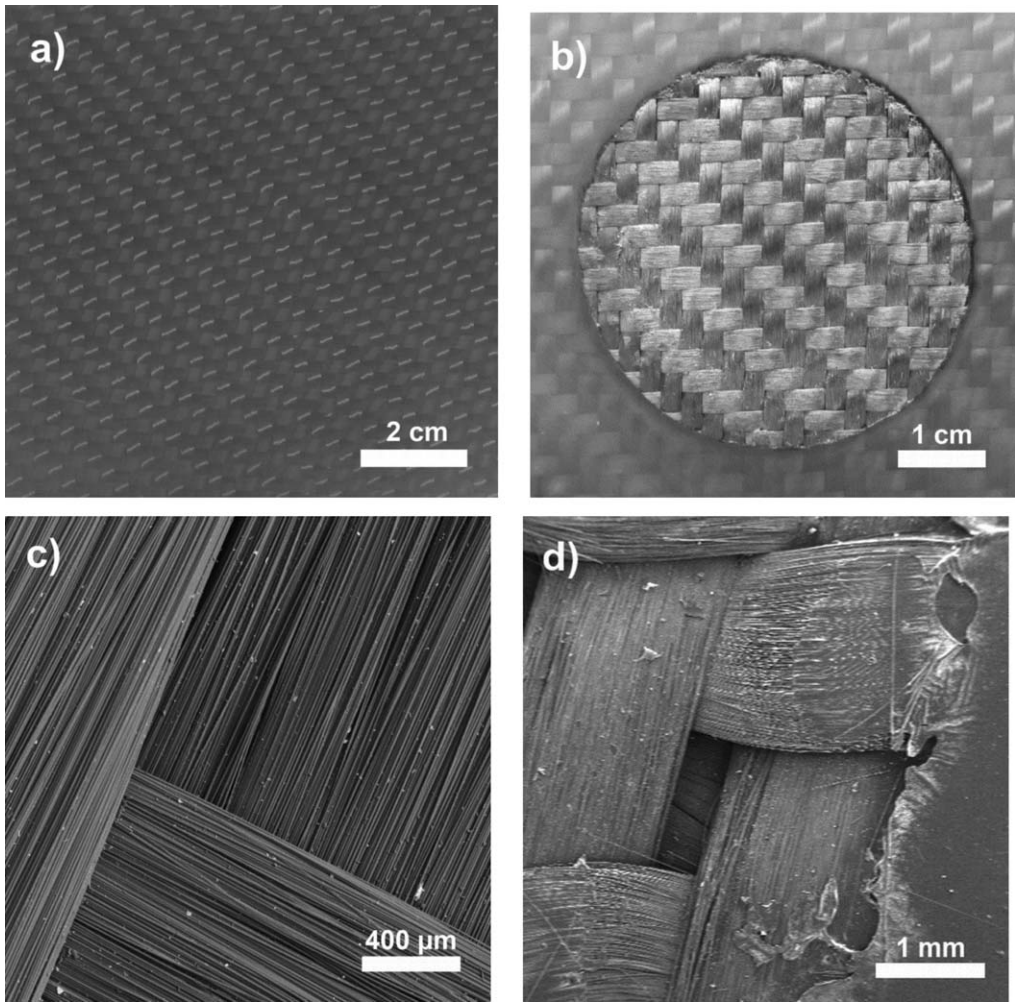

Figure 4. Images of the CFRP samples (a) before the procedure and (b) after the treatment and SEM images of the (c) roving and (d) transition region between the intact and degraded matrixes.

CFs was already decomposed at a temperature of 100°C[21,22] and were not visible because of the small percentage of the whole sample mass.

Furthermore, the complete degradation of the thermoset matrix was examined and evaluated by IR spectroscopy. Clear signals in the IR region were recognizable because of the change in the reflectivity (Figure 7).

Typical CH— and CH_2— stretching was observed between 2800 and 2900 cm^{-1}. The epoxy resin was identified by a small band of C—H oscillation, which was represented by a wavelength of

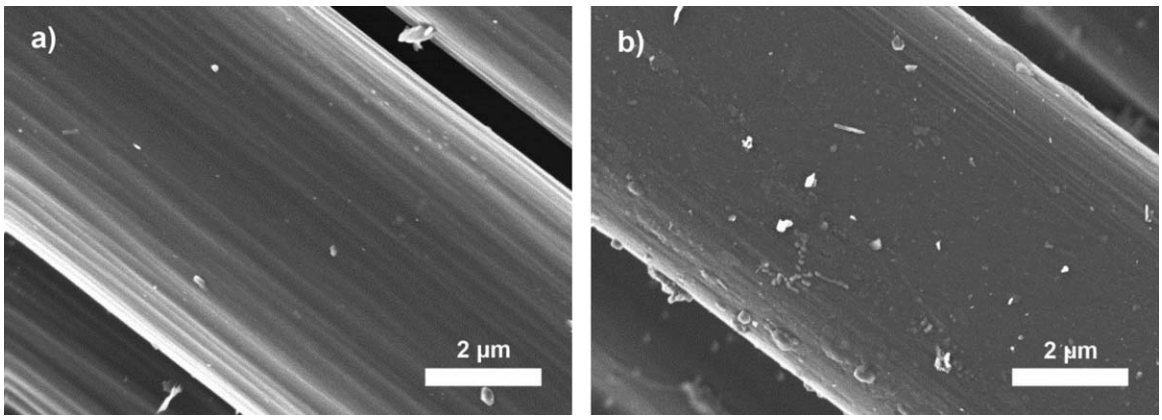

Figure 5. SEM images of CF (a) before and (b) after matrix decomposition

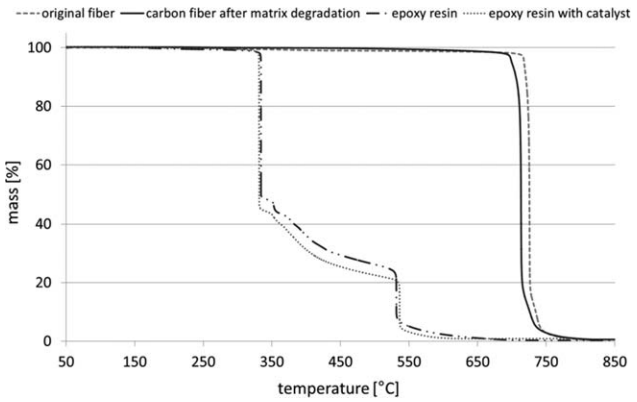

Figure 6. Characterization of the physicochemical treatment with TGA.

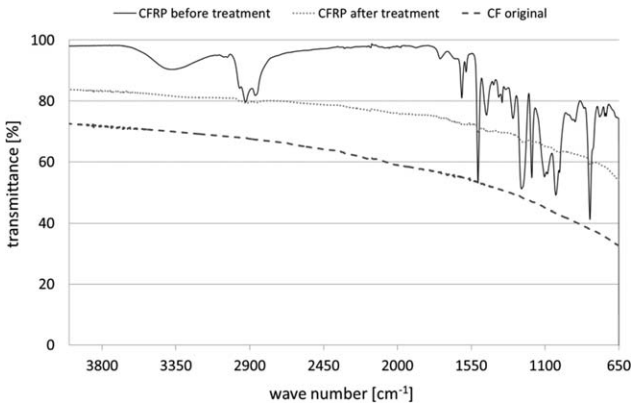

Figure 7. IR spectra before and after the physicochemical treatment.

3050 cm^{-1}. Additional information about the resin was provided at 1508 cm^{-1} by the characteristics of the aromatic groups, in particular the stretching vibrations of C—C bonding. The C—O—C stretching at 1034 and 826 cm^{-1} were associated with ether groups.[23] After 10 min of treatment with the OSC, the IR spectrum in Figure 7 was obtained, and this is illustrated by the dotted line. The spectrum exhibited a significant change in general and showed a total absence of the resin; consequently, this was typical of a spectrum of a CF without any sizing.

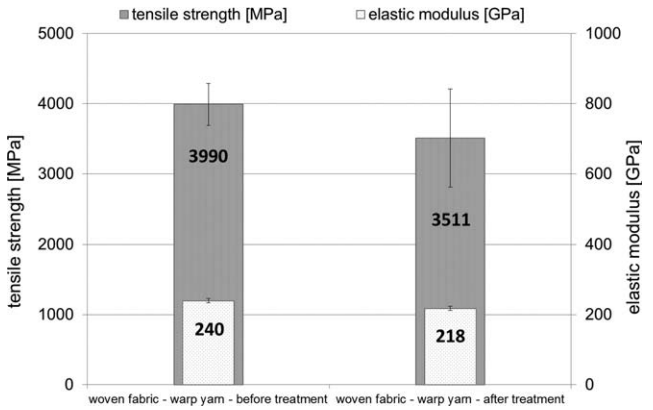

Figure 8. Single-fiber tensile tests on a fiber specimen of the textile fabric before and after matrix degradation.

Additionally, in Figure 6, it is shown that the mixture of catalyst and epoxy resin decomposed in the same way as the pure epoxy and showed no side effects. Accordingly, this proved that the IR radiation and catalyst were important for the degradation of the matrix.

Textile physical investigations of single-fiber tensile strength were also carried out (Figure 8). We observed that the single fibers of the treated composite still had a remaining tensile strength of up to 88% after matrix removal. We assumed that the loss was due to a high thermal load combined with the decomposition of the sizing; this led to reduced mechanical stability in the CFs. The elastic modulus was also affected by the treatment; this resulted in a decrease from 240 to 218 GPa (91%). From the variation, we observed that the individual fibers were affected by different intensities. The influence of the thermal treatment and the chemical interactions taking place are the topic of ongoing investigations. The subsequent aim is to develop a more controlled and gentle treatment to assure a minimum loss of textile strength of reinforcing CFs during the decomposition of the matrix.

Finally, the repair was conducted by the refilling of the treated area with epoxy resin (Figure 9). Obviously, the SCRIMP method is highly appropriate for filling the cavities of the

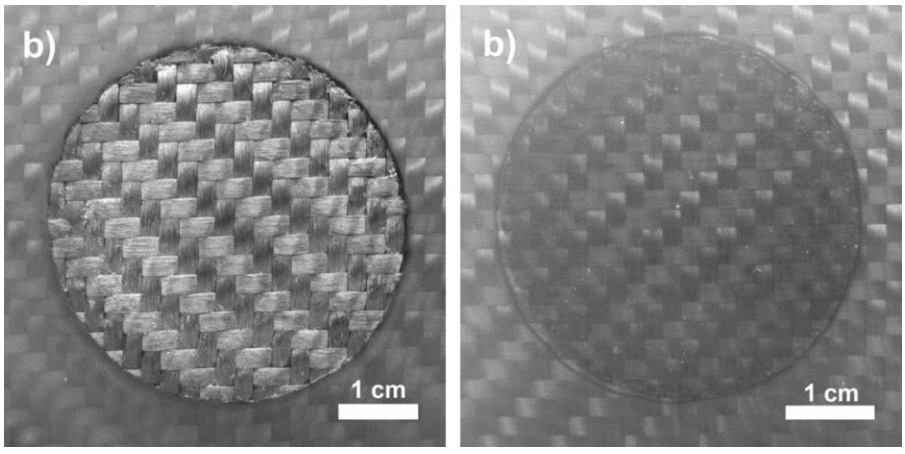

Figure 9. CFRP (a) after the removal of epoxy resin and (b) after refilling with new epoxy resin.

reinforcement fabric, which contained neither sizing nor epoxy matrix [Figure 9(a)]. According to this procedure, the specific area was fully impregnated by new resin, and the CFRP was reconstructed again [Figure 9(b)]. Nevertheless, a small but smooth interfacial area remained between the untreated and treated parts of the composite. It appeared flat, clean, and without any roughness.

CONCLUSIONS

The conduction of the complete removal of the epoxy matrix followed by a refilling with resin to regain the bearing capacity was successfully performed. We showed that a CFRP could be freed locally from the thermosetting matrix in an efficient way with OSC without damage to the embedded woven CFs, and the damaged area could be repaired through refilling with a new epoxy resin. This procedure is very promising, and the proof of principle was shown. The gentle full removal of the matrix was visualized by SEM pictures, where no major impact on the reinforcement structure was found. Additionally, the thermooxidative treatment, especially the thermal decomposition of the epoxy resin, was proven by attenuated total reflectance–IR and TGA measurements. The physicochemical treatment as part of the concept for CFRP repair led to new possibilities in direct competition to common repair procedures. Furthermore, the local repair concept promises a high cost effectiveness in comparison to the replacement of complete CFRP structural elements, and it comes along with an easy handling of the procedure itself. Nevertheless, further investigations are currently the focus of our research, especially with regard to the uniformity of the treatment across the irradiated area and the further reduction of the fiber damage.

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