CHANGES IN FIRST-PLY-FAILURE MODE OF THERMALLY DEGRADED CFRP

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Abstract
Composite structures are usually not meant to be used at temperatures exceeding a certain temperature limit. However, accidental overheating can never be excluded, e.g. due to hot exhaust gases, malfunctions in electric equipment or leaky heating pipes. Predicting heat damages in carbon-fibre-reinforced-polymer (CFRP) has been the subject of several detailed investigations. Once heat damage occurs in the material, it could progress quickly, which could lead to failure. For that reason, detection of first damages caused by heat, such as transverse matrix cracks, is very important. Acoustic emission (AE) analysis provides an insight into damage development in composites, thus gives the opportunity for understanding failure mechanisms of composites.

CFRP panels are exposed to heat above maximum operational temperature at various durations. Thermal degradation of the material is microscopically observed and the degradation of the tensile behavior is characterized over time using passive AE analysis and infrared spectroscopy. The onset of the failure is identified using AE analysis. First results show that the development and propagation of cracks depend on the level of thermal degradation and the fiber orientation to the applied load. Already existing cracks due to the thermal degradation lead to a quicker crack propagation at relatively small loads.

1. Introduction

Damage caused by thermal load can have a great influence on mechanical properties over the lifetime of a composite material. Once damage occurs in the material, it can progress quickly. Transverse matrix cracking is considered as one of the initiating modes that lead to failure. For analyzing crack initiation or propagation in a composite material, acoustic emission testing (AET) is a powerful method [1, 2]. The damage creates a displacement on the surface (acoustic emission source), where energy is rapidly released. This causes an elastic wave that can be detected by the sensor. AET can also be used to locate the acoustic emission source in real-time.

Even though CFRPs have been in use for many years, very limited data is available on the behaviour of the material regarding thermal loading. When heating the material above the glass transition temperature, thermo-mechanical effects may occur due to softening and/or decomposition of the polymer. Degradation is even more crucial when heating of the material occurs in an oxidizing environment than in vacuum or inert atmosphere [3, 4]. Investigations have shown that matrix cracking and delamination, as well as a degradation of the interphase at aging temperatures in the ranges of the glass transition temperature occur after thermal exposures [5, 6]. It was also found that the mechanical properties like tensile, compression or shear strength can be reduced severally by thermal degradation [6].

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Methods to evaluate degradation effects are preferably easy, fast, non-destructive and of unambiguous significance [7]. Micro-Attenuated Total Reflection Fourier-Transform Infrared (µ-ATR-FTIR) spectroscopy is widely used to pursue polymer matrix decomposition [8-10]. In previous works [11, 12] an empirical correlation was established between the degradation of the polymer matrix traced by infrared spectroscopy and the residual mechanical strength. For HexPly® 8552/IM7 a correlation in the range of the glass transition temperature (180 to 200°C) was reported [13]. With these methods it was not possible to determine the exact temperature and duration of the thermal pre-load, as the thermal damage is a product of both. In [14] new techniques were proposed to separately determine temperature and duration of a thermal pre-load with focus on long term degradation. In this study degradation temperatures up to 340°C were used.

The goal of this study is to observe the onset of crack propagation of thermally degraded CFRP under tensile loading by using AE analysis. The thermal degradation of the material is microscopically observed and characterized versus storage time with help of µ-ATR_FTIR spectroscopy.

2. Material

All tests were conducted using the carbon fiber reinforced epoxy system HexPly© 8552/IM7 from Hexcel. The matrix system 8552 consists of aromatic epoxy resins, which are toughened with temperature resistant thermoplastic polyethersulfone. The laminates were cured in an autoclave according to the manufacture's data sheets. The laminates consisted of 16 unidirectional (UD) plies with a quasi-isotropic (QI) lay-up $[45/90/-45/0/0/-45/90/45]_S$.

In order to ensure that the laminates did not have any defects, all laminates were visually inspected for surface defects and ultrasonic C-scans were performed to assure that the material is free of internal delamination, voids or deviations of the fiber orientation prior to testing.

3. Experimental

The samples with a dimension of approximately 300 mm x 300 mm were isothermally degraded in standard convection ovens at three different temperatures: 180°C, 190°C, and 200°C for up to 195 days. In order to obtain different states of degradation, individual laminates were taken out of the ovens at pre-determined release dates. After thermal aging glass fiber reinforced end tabs were applied and the laminates were cut into 300 mm x 30 mm specimens using a water-cooled diamond wheel saw.

After being cut, the specimens were dried at 70°C to assure the same conditions for all specimens. When dried, tensile tests with a cross head-speed of 1 mm/min were performed. During tensile testing, the strain was measured by a clip gauge and the damage was monitored using an AET system (Vallen Systeme, Germany). The specimens were only loaded until AE signals indicated damage propagation and not until rupture occurs. After indication of damage propagation were detected, analysis of tests were performed.

Changes in composition of the polymer matrix were analyzed by µ-ATR-FTIR spectroscopy (Bruker, USA). Also the surfaces and cross-sections were investigated using scanning electron microscopy (SEM). In order to inspect the cross-sections microscopically, the samples were embedded in epoxy resin and polished.

4. Results

4.1 SEM Analysis

SEM investigations were performed to analyze the thermally degraded specimens' surface for cracks. At 180°C first cracks on the surface can be observed after 14 days, and for 190°C first cracks were visible after 5 days. The earlier appearance of cracks at a temperature of 190°C can be explained by a

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faster degradation on the surface due to a higher temperature. The initial formation of cracks for an aging temperature of 200°C appears after 50 days. The delay can be explained by the transition of the material at that temperature. At 200°C the material (cured at 180°C) changes from the energy elastic state to the entropy elastic state to a much more ductile behavior. All cracks proceed primarily parallel to the fiber orientation of the outermost ply (Figure 2).

In Figure 1 a non-thermally degraded surface is shown as a reference. As expected, no cracks on the surface were found. The clearly visible linear embossed structures on the surface are the negative imprints from the peel-ply. Figure 2 shows a SEM photograph of a specimen thermally degraded at 180°C for 195 days. Matrix cracking downward an angle of 45°can be observed.

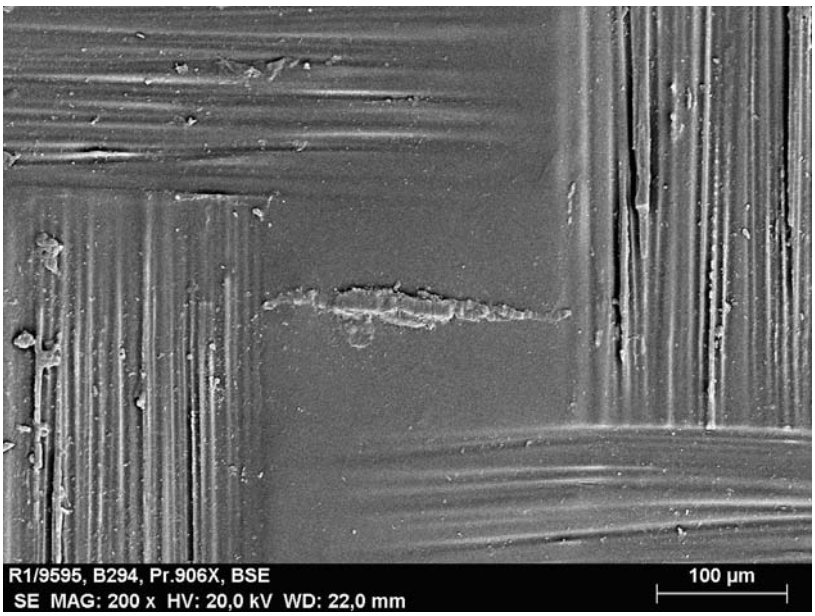

Figure 1: SEM photograph; non-thermally degraded surface of a specimen showing no cracks parallel to the outermost ply

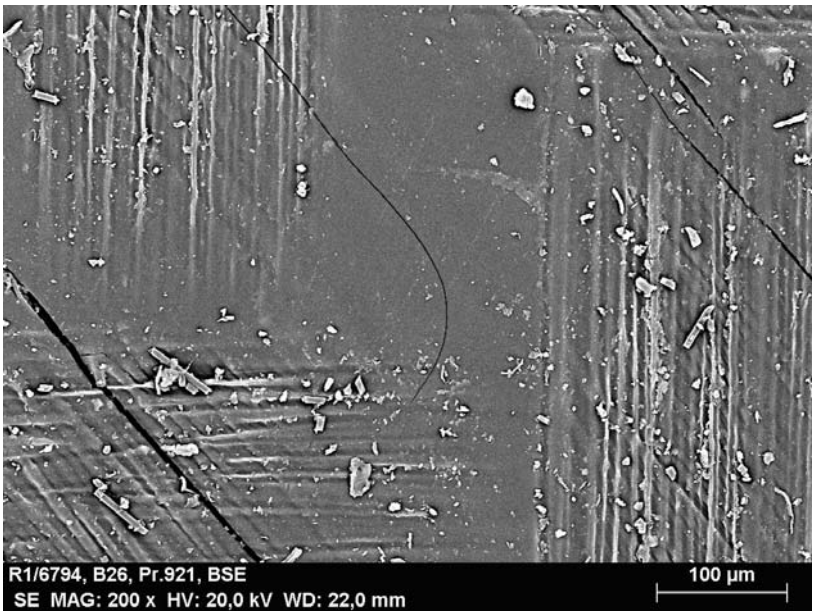

Figure 2: SEM photograph; degraded at 180°C for 195 days showing cracks on the outermost ply

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Figure 3 shows a detailed part of the cross-section of a specimen thermally degraded for 195 days at 180°C. It can be seen that fine structured cracks on the surface area have developed. Cracks can be found in the resin rich zone of the surface (A) as well as intralaminar cracks close to the surface (B) (cracks are marked with an arrow). In order to characterize crack propagation once mechanical load is applied, selected thermally degraded specimens were mechanically loaded up to an axial strain of 0.3 %. After mechanical loading the specimens were then analyzed by SEM. Figure 4 shows a detailed part of the cross-section of a specimen thermally degraded at 180°C for 195 days and loaded in tensile mode with 0.3% maximum strain. Now, compared to Figure 3, a crack with an extension across the complete first ply can be found (marked with a white arrow). This clearly shows that cracks induced by thermal degradation can still propagate during mechanical loading.

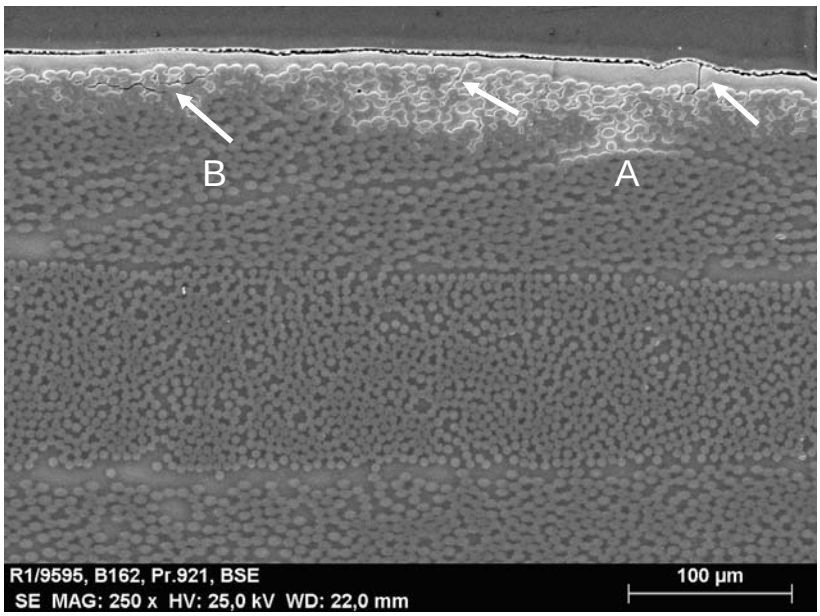

Figure 3: SEM photograph; zooming part of the cross-section of a specimen thermally degraded at 180°C for 195 days

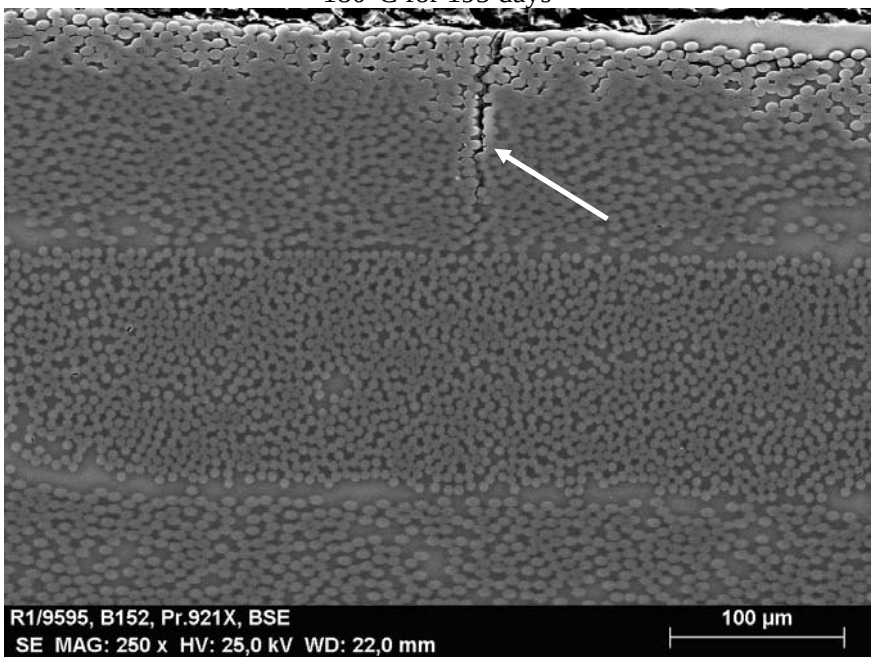

Figure 4: SEM photograph; zooming part of the cross-section of a specimen thermally degraded at 180° for 195 days and loaded in tensile mode with 0.3% strain

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4.2 AET during Tensile Loading

Specimens were loaded in tensile mode until the AET indicated multiple damages. Figure 5 shows a stress-strain-diagram including the simultaneously recorded AE-signals of a none-thermally degraded specimen. An almost linear stress-strain–relationship can be observed. The first significant AET energy peak occurs at a strain of approximately 0.41 %. The AE event and the corresponding strain are marked in the diagram. The energy signals shown in the figures do not represent energy in the sense of a physical unit, merely an electrically gained signal without physical unit.

In Figure 6 a stress-strain-diagram including the simultaneously recorded AE-signals are shown for a specimen thermally degraded at 180°C for 195 days. Again, the stress-strain behavior is almost linear. The first significant AE energy peak occurs at a strain of approximately 0.15 %. Compared to the non-thermally degraded specimen, the AE events appear at much lower strains due to the earlier propagation of already existing cracks.

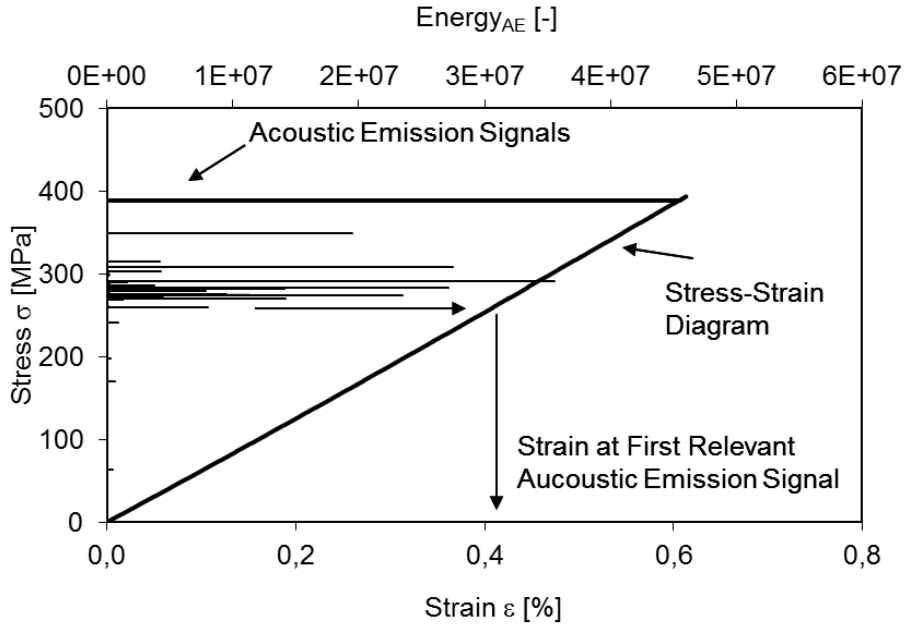

Figure 5: Non-thermally degraded; stress-strain diagram and acoustic emission signals

4.3 Characterization of Thermal Degradation Using µ-ATR-FTIR Spectroscopy

Using µ-ATR_FTIR spectroscopy to analyze the 8552 matrix system, intensive bands occur at a wavelength bands of 1610 cm^{-1} and 1510 cm^{-1}, which are attributed to the epoxy resin. The bands at 1579 cm^{-1} and 1486 cm^{-1} are characterized to the polyethersulfone. Detailed interpretation of the components is given in references [5, 14, 15]. In order to evaluate the IR intensity ratio of the epoxy resin and the polyethersulfone the band 1510 cm^{-1} was chosen for the epoxy resin, and 1486 cm^{-1} was chosen for the polyethersulfone. The spectra were taken on the surface of the specimens. An intensity ratio of 1 represents a non-degraded specimen.

Figure 8 shows the decline of intensity ratio over the degradation times. The longer thermally loaded, the more the intensity ratio decreases. It is also visible that a higher temperature results in a faster degradation or that long time degradation at lower temperatures leads to the same degradation as degrading for a shorter time and higher temperatures.

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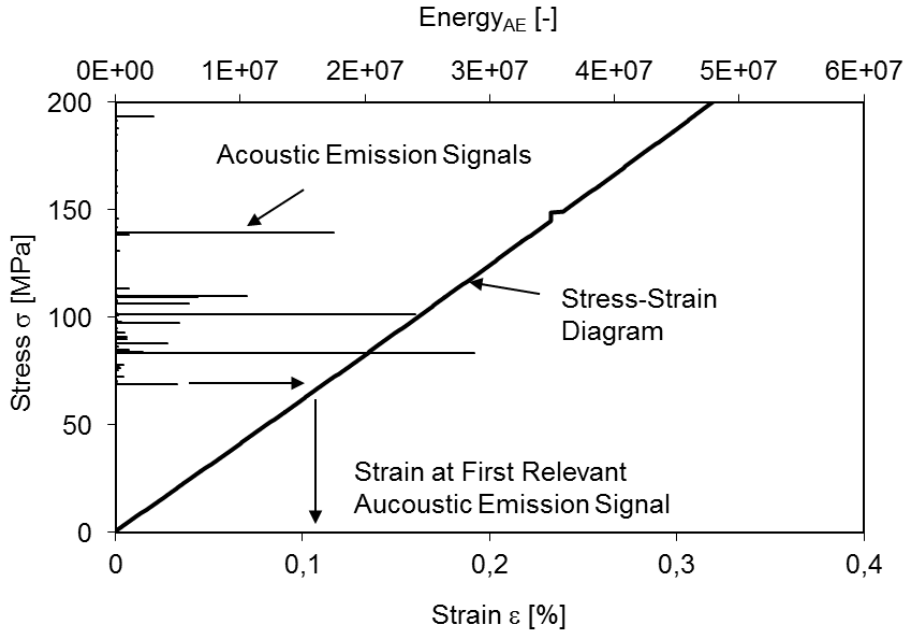

Figure 6: Thermally degraded at 200°C for 195 days, stress-strain diagram and acoustic emission signals

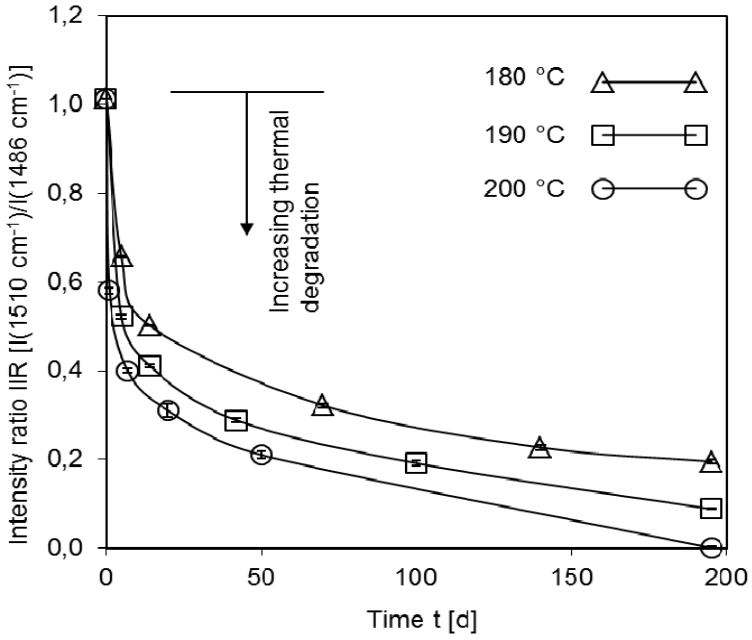

Figure 7: Intensity ratio vs. storage time of thermal degradation

4.4 Interrelationship between thermal degradation and initial crack propagation for the different fibre orientations

In Figure 7 the first significant AE energy peak stains are plotted as a function of the thermal degradation determined by IR spectroscopy for. Increasing degradation is plotted versus the intensity ratios from 1 to 0 (degradation grows towards 0). The first significant AE energy peaks at an intensity ratio of 1 (no thermal degradation) occurred at strain of approximately 0.41 %.

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Looking at the intensity ratios of the infrared spectroscopy and the acoustic emission signals, a decline of the strain at which first AE energy peaks can be observed with increasing thermal degradation. However, different aging temperatures have no significant influence on the results, since lower temperatures at longer storage time have a similar effect as higher temperatures at shorter storage time.

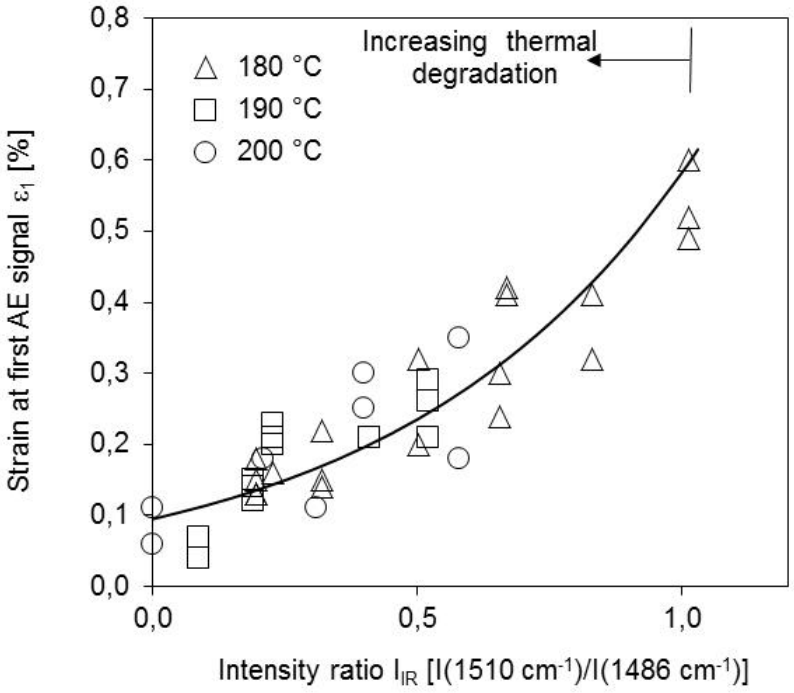

Figure 8: Evaluated strain at first significant acoustic emission energy peak at all three aging temperatures vs. thermal degradation characterized by IR intensity ratio

5. Conclusions

The goal of these investigations was to observe the onset of crack propagation of increasingly thermally degraded CFRP under tensile loading by using AE analysis. Thermal degradation was interpreted microscopically and µ-ATR-FTIR spectroscopy was used to analyze chemical degradation of the matrix. Due to thermal degradation the formation of cracks with low penetration depth can be observed on the specimens' surface. The cracks propagate mainly parallel to the fiber orientation of the outermost ply and with increasing degradation a growing number of cracks can be observed. In order to characterize how the thermally induced cracks behave after mechanical load, degraded specimens were loaded in tensile mode up to a strain of 0.41 %. After the mechanical load was applied, crack growth took palce.

In order to detect the onset of crack propagation, specimens were loaded in tensile mode until the AET indicated multiple damages in the specimen. Using AET it was possible to determine the first significant crack growth or the development of new cracks during tensile loading. The first significant AE energy peaks (crack growth) were plotted as a function of the thermal degradation determined by µ-ATR-FTIR spectroscopy. A decline of the strain at which first AE energy peaks could be observed with increasing thermal degradation.

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