Effect of Thermal Treatment on CFRP Parts Before and After Adhesive Bonding

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Abstract: Numerous non-destructive techniques are being investigated for assuring quality of the adhesive bonds. The research presented here is focused on non-destructive assessment of carbon fibre reinforced polymer (CFRP) parts. The surface condition directly influences the performance of adhesive bonds. The structural joints should ensure safe usage of a structure. However, some modifications of the surface may lead to weak bond that cannot carry the desired load. This is why there is a search for methods of surface assessment before bonding. Moreover, reliable techniques are required to allow to verify the integrity of the adhesive bond after manufacturing or bonded repair. We focus on the laser induced fluorescence (LIF) method for assessing the surface state. The LIF is a non-contact measurement method. In the context of adhesive bond assessment the electromechanical impedance (EMI) method is studied. The EMI uses surface bonded piezoelectric sensors for excitation and sensing. The investigated samples were made of CFRP layers. The samples were treated at elevated temperatures. The influence of the thermal treatment was studied using LIF. The thermal treatment at 220 ℃ could be clearly distinguishedrom the rest of the considered samples. The thermally treated plates were bonded to untreated plate and then they were measured with the EMI method to study the influence of the treatment on the adhesive bond. The changes of EMI spectra were significant for the treatment at 280 ℃ and for some thermally treated samples that were later contaminated with de-icing fluid.

Key words: adhesive joints; carbon fibre reinforced polymer (FRP) composite laminates; composite materials and repairs; composites; electromechanical impedance; non-destructive testing (NDT)

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0 Introduction

The research presented here is focused on non-destructive assessment of surface before bonding and the adhesive bonds of carbon fibre reinforced polymer (CFRP) parts. The structural joints should ensure safe usage of a structure. The performance of adhesive bonds depends on the properties of the surfaces to be joint. Some modifications of the surface may lead to weak bond that cannot carry the desired load. It is important to have a reliable tool that allows to assure the quality of the surface prepared for bonding. One of the promising methods for surface assessment is the electronic nose[1]. Apart from the problem of surface assessment, another important subject is to assess the bonded part. The examples of techniques investigated for this task are electromechanical impedance[2] and laser-induced shock waves[3]. The research reported here aims at non-destructive assess of the surface with pre-bond modifications related to conditions encountered during the in-service life of composite parts. The pre-bond modifications have an influence on the fracture toughness of the CFRP bonded joints. Markatos et al. studied the influence of pre-bond release agent contamination and moisture absorption on mode-I fracture toughness of

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CFRP bonded joints[4]. A mode-I double cantilever beam specimen was used to determine the mode-I energy release rate (GIC) referring to crack initiation. The lowest considered contamination with release agent did not affect the bond. The increase of the contamination caused at least 60 % drop of the GIC value in relation to the reference case. The pre-bond thermal treatment results reported in the literature show that the GIC value decreases by 10% and 13 % for treatment at 190 and 200 ℃, respectively[5]. In the case of treatment at 210 ℃ the increase by 9% was observed[5]. The de-icing fluid contamination has a negative effect on both mode I and mode II fracture toughness of the bonded joints[6]. With increasing the contamination level, the mode I and mode II critical energy release rates decrease. Published investigations on contamination with Skydrol hydraulic fluid showed that there is a considerable influence on the fracture toughness of the joints[7]: It decreases by 27%.

The intention of this paper is to study pre- and post-bond effects of thermal treatment. The laser induced fluorescence (LIF) method was used for assessment of the surface condition. The LIF method is a spectroscopic method that can be potentially applied to large surface material analysis[8]. The detection of kerosene and hydraulic fluid on CFRP surface was reported before[9]. Good results were obtained for 266 nm excitation. In other work[10] three wavelengths were studied (266, 355 and 532 nm). Detection of hydraulic fluid, release agent and moisture contaminations, and thermal treatment were presented. It was shown that at 532 nm the thermal treatment can be easily distinguished from the remaining cases. Moreover, it was presented that samples treated at 190 ℃, 200 ℃, and 210 ℃ were characterized by increasing LIF intensity and could be distinguished from each other and from the referential samples. In research reported here we present results for higher temperatures (220 ℃, 260 ℃ and 280 ℃). Moreover, a combined case is considered with thermal treatment and surface contamination with de-icing fluid. The adhesive bonding is investigated by the electromechanical impedance (EMI) method. The EMI method is considered as one of the non-destructive testing (NDT) or structural health monitoring (SHM) methods. The EMI principle is based on a piezoelectric sensor that is bonded to the inspected structure. During the measurement, electric quantities of the sensor are gathered for selected frequency band. The EMI was studied in the past for adhesive bonds influence by contaminants[2,11]. In particular the thermal treatment was analyzed but by using the root mean square (RMS) values and conductance maximum shift in 3—5 MHz range[11].

In comparison to previously published results the novelty of the paper is as follows:

(1) CFRP composites are investigated with material and lay-up different from those in Refs. [2,10].

(2) Adhesive was different from in Ref. [2].

(3) Frechet distance[12] is used for assessment of the thermal treatment influence on the adhesive bond.

(4) Mixed modifications of surface is considered: The samples are thermally treated and then contaminated with the de-icing fluid.

1 Samples and Methods

1.1 Samples

The samples under investigation were made of Hexcel M21E/IMA material. The samples for surface assessment with LIF were single plates made of 8 plies and layup sequence: $[0, 0, 45, -45]_S$. Their size was 200 mm×200 mm. The samples for adhesive bonds assessment comprised of two plates with the same layup sequence adhesively bonded together. The bonded sample size was 100 mm×100 mm. The plates were bonded with FM 300-2 adhesive cured at 121 ℃. The frame of the study is presented in Fig. 1. Total 30 samples were investigated. Twelve samples for surface assessment comprised of three reference samples (RREx) and nine thermally treated sam-

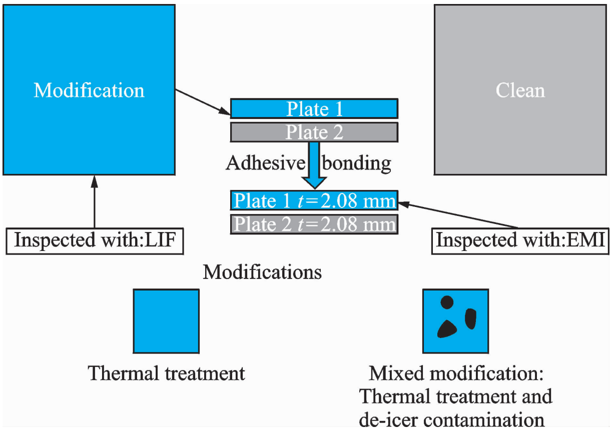

Fig. 1 Overall concept of the pre- and post-bond inspection of the CFRP samples

ples. The thermally treated samples were hold in air circulation oven for 2 h. Three levels of thermal treatment were investigated. Three samples were treated at 220 ℃ (RTD1x), three at 260 ℃ (RTD2x) and three at 280 ℃ (RTD3x). This case simulated real situation that structural parts may be exposed to external heat source or lightening impact. High temperatures can cause local overheating and damage the resin. It leads to a loss of the mechanical properties of the CFRP structure and bonded repair can also be affected. Next, six samples were prepared with mixed modifications. It means that after thermal treatment (at 220 ℃) the samples were contaminated with de-icing fluid. The contamination case with de-icer (DI) was prepared by dip coating of the plates in a water solution of the de-icer with two concentrations. The SAFEWAY KF de-icer was used. After dip coating the samples were dried in the oven for 2 h at 40 ℃. Acclimatization at room temperature was allowed for at least 24 h. The dip coating results were controlled by XPS measurements and potassium content was taken as an indicator of the contamination level[11]. The sample with symbol RTD1DI1x had the contamination on the level of 6.4 at.% K, while the samples RTD1DI2x contamination was 10.9 at.% K. The used de-icer was a runway de-icing fluid that can affect the aircraft parts. After drying, the potassium formate, which was present in the de-icing fluid, formed a thin layer on the CFRP. When cleaning the aircraft before a repair, this fluid can be transported to bonding areas and contaminate the bond. This may lead to a weak adhesive bond.

The same scheme of treatment and contamination was followed for adhesively bonded samples. The bonded reference samples comprised of two plates without any thermal treatment. The modified bonded samples comprised of one plate after modification (only thermal treatment or thermal treatment with contamination) and one without any treatment.

1.2 LIF method

In-situ examination of large surface materials, like fibre reinforced composites, need special methods. The analytical methods should be non-destructive, enabling large surface analysis in relatively short time. LIF is a reasonable choice. This technique allows to analyze large objects using surface scanning technique. LIF is a technique based on the analysis of spontaneous emission of atoms or molecules excited with laser, where analyzed material can be in a gas, liquid or solid state phase. Typical instrumentation for LIF analysis consists of laser illuminating investigated material and the detection system for recording fluorescence. Depending of the chemical composition of analyzed material, laser can be tuned to match the wavelength to the absorption lines or bands of specified atoms or molecules and produce an electronically excited states that can radiate.

In this paper, LIF spectra were recorded using laboratory system. The samples excitation was provided by cw DPSS Nd:YAG laser operating at 532 nm (Spectra Physics). Laser power was set to 0.2 W and laser intensity was 1 W/cm^2 (5 mm laser spot diameter). The spectra of the laser-induced fluorescence (LIF) were recorded in time integration mode. The emission spectra were dispersed by the 0.3 m spectrograph SR-303i equipped with gratings of 600 and 150 grooves/mm and coupled to the time-gated ICCD camera DH 740 (Andor Tech). Spectra were acquired in the range of 300—800 nm with resolutions of 0. 3 nm or 1. 2 nm. The measurement set-up is depicted in Fig. 2, where green excitation light (532 nm) is seen illuminating CFRP sample surface, and detector is above the sample.

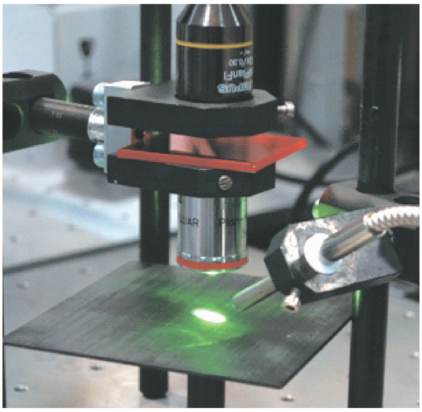

Fig. 2 Laboratory equipment for measuring of LIF spectra

The presented work here follows the previous promising results[10]. As it was shown the most effective excitation wavelength for thermal treatment assessment is 532 nm and this is used here. At the surface of each sample, 10 measurements points are randomly chosen. Such measurement points selection allow for investigation of the variability of the intensity across the samples′ surface. At each point, 10 spectra are gathered and the mean was calculated.

1.3 EMI method

The EMI method is considered as one of the NDT and SHM methods. The method principle is based on a piezoelectric sensor that is bonded to the inspected structure. During the measurement, electric quantities of the sensor are gathered for selected frequency band. The examples of investigated quantities are resistance, conductance, reactance or absolute value of the impedance. Due to direct and converse piezoelectric effect, the sensor excites the structure and senses the response from it. This electromechanical coupling causes the registered impedance spectra modification by the presence of the host structure. Various structural factors can influence the registered spectra. Appearance of additional resonance peaks, peak shift in frequency or magnitude change can be treated as indicators of defect of the structure. In order to extract damage related features for the EMI spectra, various frequency bands are analyzed. These bands depend on the inspected structure, the used piezoelectric sensor and the abilities of the available equipment. In this paper we focus on frequency band from 3—5 MHz. The band was selected as symmetric around the thickness resonance frequency of the used transducer. In the present work admittance (Y) was investigated on a complex plane. The measurements were conducted by gluing a single piezoelectric sensor per sample at the middle of the sample surface.

The admittance characteristic on complex plane comprise of G (conductance) on the horizontal axis (real) and the B (susceptance) on the vertical axis (imaginary). The proposed comparison index is based on Frechet distance (FD). FD is the minimum distance required to connect two points constrained on two separate paths, as the points travel without back-tracking along their respective curves from one endpoint to the other[7]. The definition is symmetric with respect to the two curves. The promising results of using FD to assessment of adhesive bonds contaminated with release agent was presented in Ref. [13].

2 Results

2.1 Observations using LIF method

The results for thermally treated samples assessed with LIF method are presented in Fig. 3. There are high intensity values for the first level (RTD1x) of treatment. This case corresponds to keeping the samples at 220 ℃ in an oven. The samples TD2x and TD3x were treated at higher temperatures and there is no correlation of the intensity with the used temperature. Moreover, the response is very uniform. All the six samples have comparable level of mean intensity and the standard deviation is low.

In Ref. [10] we saw a good detection of TD

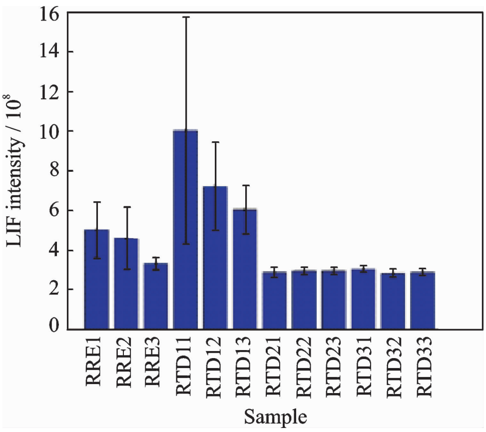

Fig. 3 LIF method results for thermal treatment (RTD)

scenario with the LIF intensity measurement at 532 nm excitation. Different levels of thermal treatment correlated with the intensity. The intensity value was growing with the growing temperature of treatment. Here we can see different behaviour. The first important difference is that the new samples (RTD) are made of different prepregs. Moreover the RTD samples were ground down to the fibres. The samples previously investigated were measured just after the thermal treatment without any surface modification afterwards (grindng, etc.)[10]. The third important difference is that the RTD samples were treated at higher temperatures than before, while the other side of the sample was not prepared/modified in any way, so we can expect only influence of the temperature of the treatment. It was decided to measure this second side and compare the results with the previously obtained (Fig. 3). The new result is presented in Fig. 4. Again the highest intensity is observed for RTD1x samples. The RTD2x and RTD3x samples have intensity values on the level of reference samples. There is also a clear difference in vertical scale between Fig. 3 and Fig. 4. This must be related to the considerable time interval between these two measurements. Recalling the previously published results[10], there was a clear intensity increase up to 210 ℃, while in this study, an increase is also observed but for 220 ℃. It seems that for 260 ℃ and 280 ℃, fluorescence is not observed in the considered bandwidth.

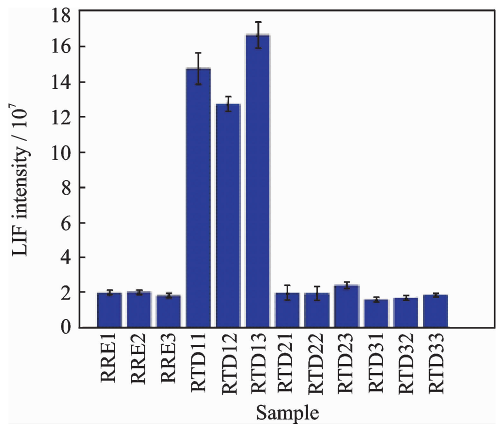

Fig. 4 Results for thermal degradation (RTD)(fluorescence intensity measured on the back face)

Knowing that the 220 ℃ case can be detected and distinguished for the remaining cases, another set of samples was prepared treated at the same temperature and contaminated afterwards with the de-icing fluid. Fig. 5 presents the results for new set of samples with mixed modification (RTD1DIxy) in comparison with the clean reference samples (RREx) and samples only after thermal treatment (RTD1x). The first observation is that the mixed modification was detected. It clearly differ from the reference. The higher level of de-icer (DI2) contamination is not related to any increase or decrease in relation to the lower level (DI1). What we can observe is that the intensities for the samples with mixed modification have higher values that for the pure thermal treatment (RTD1x). However, considering the

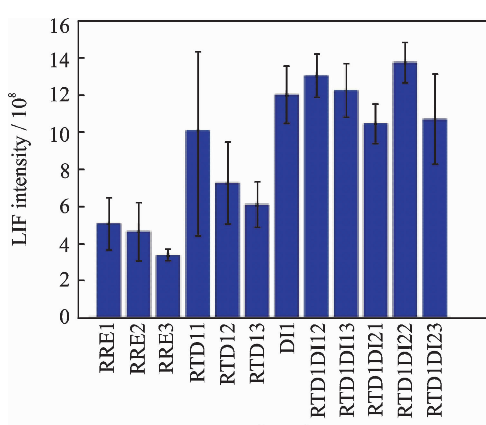

Fig. 5 LIF results for mixed modifications of the surface compared with the thermal treatment at first level and referential results

standard deviations, all the results after modifications (RTD1x and RTD1DIxy) lie within the boundaries of standard deviation for the RTD11 case.

2.2 Observations using EMI method

The results of calculating the FD value is depicted in Fig. 6 in a matrix form. It is symmetrical along the diagonal. Not all the results for measured samples are depicted here. After inspecting the spectra of free sensors and spectra obtained for the investigated samples, it was observed that for some samples the spectra look different. In some cases, the conductance maximum at about 4 MHz was not apparent or the peak magnitude increased after the sensor bonding to the sample. Total four such cases were identified and they were not analysed to avoid misinterpretation of the results, because the observed anomalies could be related to improper bonding of the piezoelectric sensors. Following samples were not considered further: RRE2, RTD12, RTD22, and RTD33. The main observation from the obtained matrix (Fig. 6) is that there is a clearer difference between the two samples, RTD31 and RTD32, and the rest of the samples. These two samples were treated with the highest temperature (280 ℃). The differences between the remaining part of the samples are not so evident. The exception is the RTD11 sample. In order to visualize the obtained results, a clearer slice of the matrix plot was presented in Fig. 7. It presents the results in relation to RRE1 sample. Small difference between reference samples is visible and the largest values of FD are observed for RTD31 and RTD32 samples. The difference between RTD31 and RTD32 samples could be caused by the difference of the samples and other factors. As it was shown before the RTD31 sample has a delamination in one of the plates[11].

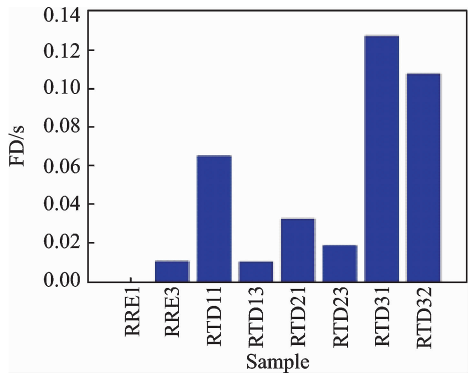

Fig. 7 FD calculated for all samples in relation to RRE1 sample

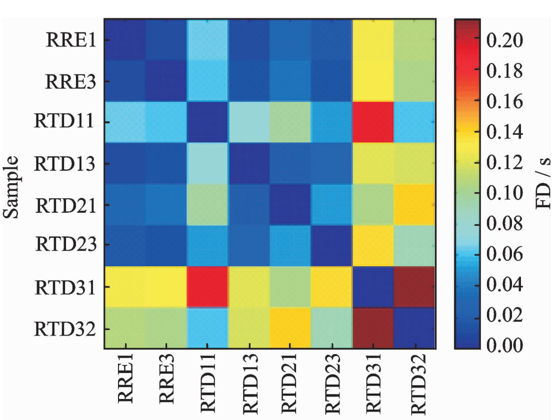

Fig. 6 FD calculated for the reference and thermally treated samples in 3—5 MHz bandwidth

The same analysis procedure as above was presented for samples with mixed modifications (RTD1Dixy). The result is plotted in Fig. 8. The RTD1x samples were plotted as well, for comparison. There is a significant high value observed for one of the samples with the highest level of modification (RTD1DI21). This is even more visible in the slice plot presented in Fig. 9. Most of the samples with mixed modifications (except RTD1DI11 and RTD1DI12) have higher FD values than the reference samples and the RTD1x

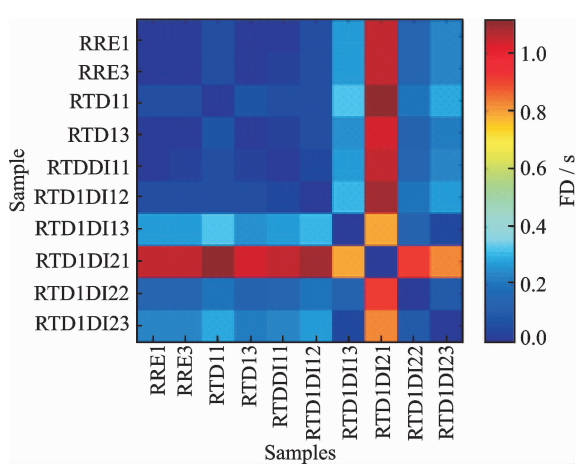

Fig. 8 FD calculated for the reference and thermally treated samples at first level with mixed modification (3—5 MHz bandwidth)

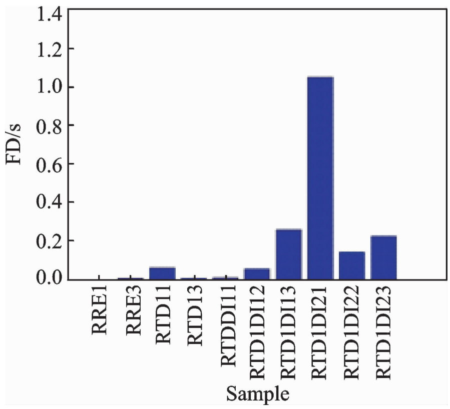

Fig. 9 FD calculated for RTD1x and RTD1Dixy samples in relation to RRE1 sample

samples.

3 Conclusions

The samples thermally treated at 220 ℃ (RTD1x) are characterized with high level of LIF intensity in comparison to reference samples and samples treated at 260 ℃ and 280 ℃. The higher intensity values were observed for measurement on both sides of the samples. Above 220 ℃, the LIF intensity presented results comparable to reference samples. The thermal treatment level could not be determined for the considered cases. Taking into account the results presented in this paper and those in Ref. [10] it can be concluded that thermal degradation up to 220 ℃ can be distinguished. Moreover, it was shown that the detection of 220 ℃ was possible even if the surface was contaminated afterwards with the de-icing fluid.

Assessment of the bonded samples with EMI allowed clear separation of the samples treated at the highest considered temperature (280 ℃) and most of the samples with mixed modifications comprised of thermal treatment and de-icer contamination.

The research will be continued with different types of pre-bond surface modifications.

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