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Spectroscopic evaluation of structural changes in composite materials subjected to self-heating effect

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ABSTRACT

Due to their excellent mechanical properties and low weight, polymer composites have gained a lot of attraction as materials for numerous engineering applications. Many of these machine components are, however, subjected to intensive loading and vibrations, which may lead to the occurrence of a self-heating effect. This can further enhance the fatigue process and result in the significant intensification of structural degradation, *e.g.* matrix and interface cracks, as well as delamination. The self-heating effect should be, therefore, considered as a serious concern wherever the polymer composite elements are applied. In our study, we focus on the extensive evaluation of the consequences of self-heating effect for the structural and chemical degradation of polymer composite materials. Microscopic and spectroscopic techniques are applied to evaluate the results of self-heating effect on the series of glass fiber reinforced polymer specimens subjected to cyclic mechanical loading. As the result, we provide the range of self-heating temperature values, for which the beneficial residual cross-linking reactions dominate over the concurrent thermal degradation processes.

1. Introduction

Due to their excellent mechanical properties and low density when compared with traditional steel and other metal-based construction materials, polymer composites have gained a lot of attraction as materials for engineering constructions, especially in land, marine and air means of transport [1–4]. Many of these machine elements are subjected to intensive loading and vibrations, which may lead to the hysteresis phenomenon occurring due to out-of-phase oscillations between stress and strain magnitudes. As the result, the most of generated energy is dissipated as heat and the temperature of the element increases, leading to the self-heating effect [5–8]. This fatigue-induced localized temperature rise can significantly affect the lifetime of polymers and polymer-based composites [9–12]. Some of the researchers reported unexpected increase in stability when high frequencies are applied [13]. Others, on the contrary, described the decrease in the mechanical performance due to the heat softening effects [14]. Both of these outcomes have the common origin, the self-heating effect, and this is crucial to be able to distinguish between conditions leading to the strengthening of the composite [13] and these facilitating structural degradation processes, resulting in matrix cracks, interface cracks as well as delamination. The self-heating effect should be, therefore, considered as a serious concern wherever the polymer composite elements are applied.

The effects of localized temperature rise are mainly dependent on the chemical composition of polymers forming the element subjected to fatigue. Because of their outstanding mechanical properties, high adhesion strength, good heat resistance, and high electrical resistance, epoxy resins have been widely applied as construction materials, achieving the regnant status in aircraft and aerospace engineering [15–17]. When epoxy matrix is additionally reinforced with carbon fiber, the resulting carbon fiber reinforced polymer (CFRP) exhibits superior electrical, mechanical and thermal properties [18–20]. Although epoxy resins can differ in chemical structure, being derived from bisphenol A, cycloaliphatic compounds or novolacs, for instance, what they all have in common is the presence of epoxy rings placed in both ends of the polymeric chain [16]. Responsible for the occurrence of the cross-linking reactions, epoxy moieties are present also in already cross-linked resins giving the possibility for the residual cross-linking processes to take place [8]. Under specific conditions, usually involving elevated temperatures, the presence of unreacted epoxy groups can lead to the self-healing behavior of the composite materials [21,22].

Numerous studies performed earlier by our group allowed for determination of the characteristic temperature values at which mechanical degradation starts to be observable [23–26]. This characteristic self-heating temperature is called by our group the critical self-

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heating temperature. The mentioned studies were focused firstly on the evaluation of the self-heating temperature evolution during fatigue loading with accompanying self-heating effect [23], and were recently extended with the measurements of acoustic emission, microscopic analysis of surface, residual strength of specimens subjected to self-heating at certain temperature values [24], energy dissipation rate [25], as well as quantitative analysis of occurring fatigue damage at certain values of the self-heating temperature via X-ray computed tomography [26]. This multiphysical analysis allowed getting an overview on degradation processes occurring during fatigue intensified by the non-stationary self-heating. Since the phenomenology of self-heating process has its roots at the molecular level, it is essential to investigate the criticality of the process from the chemical point of view.

In present study, we focus on the extensive evaluation of the effects of self-heating phenomenon on the structural and chemical changes of polymer composite materials. Our hypothesis states that self-healing can have either strengthening or deteriorating effects on the performance of composite material, depending on the rate of residual cross-linking reactions and concurrent thermal degradation processes. Raman spectroscopy has been chosen as the powerful tool for the monitoring of the cross-linking processes [27–29], also these occurring in the GFRP subjected to fatigue loading resulting in self-heating effect. Basing on the analysis of Raman spectra, it was possible to determine the temperature ranges in which self-heating effect could lead to self-healing of the composite as well as the temperature values resulting in the irreversible structural changes deteriorating its performance.

2. Materials and methods

2.1. Testing of self-heating effect under fatigue loading

The specimens made of 14-layered epoxy laminate reinforced by plain weave E-glass fabric with a weight of 200 g/m^2 was manufactured and supplied by Izo-Erg S.A. (Gliwice, Poland). The specific dimensions of specimens were as follows: the length of 100 mm, the width of 10 mm, and the thickness of 2.5 mm. The manufacturing process and basic material properties of tested laminate can be found in [5]. The specimens were loaded with a constant frequency of 30 Hz and the initial loading force of 90 N, until reaching the specific value of the self-heating temperature on their surface. This allowed for obtaining different stages of structural degradation of specimens caused by mechanical fatigue and the self-heating effect. The tests were performed for the maximum self-heating temperature observed on the surface in the range of 40 ÷ 110 °C. In order to ensure statistical repeatability, the tests with the same set of process parameters were performed 4 times. Prior to fatigue tests, the specimens were covered by the black matt heat-resisting enamel in order to ensure appropriate thermal emissivity for infrared radiation measurement.

The fatigue tests were performed in the fully reversed mode using own-designed laboratory test rig (Fig. 1), which was described in details in [24,26]. A specimen *5* was clamped on both sides, and the upper movable clamp *6* was connected with the electrodynamic shaker *1* through the steel stinger *3*. The shaker applied loading to a specimen. The loading signal was generated from the computer *14* and amplified by the shaker power amplifier *10* before reaching the shaker. The following parameters were measured: loading force (using the force sensor *7* placed at the upper clamp *6*), input vibration acceleration (using the accelerometer *2* placed on the table of the shaker), output vibration velocity (using the laser Doppler vibrometer (LDV) *9* focused on the surface of a specimen close to the lower clamp *4*), surface temperature distribution of a specimen (using infrared camera *8*, and acoustic emission (AE) using a probe *12* glued to the end of a specimen below the lower clamp *4* and connected to the acquisition system through the pre-amplifier *13*). In order to acquire and synchronize measurements, the sensors and LDV were connected to computers through the multichannel signal acquisition module *11*. The scheme and picture of the experimental test rig used for fatigue tests are presented in Fig. 1.

2.2. Spectroscopic and microscopic testing procedures

The changes in chemical structure of epoxy-based reinforced composite specimens subjected to fatigue testing were characterized by means of Raman spectroscopy using Renishaw InVia confocal microRaman system equipped with laser source operating at 830 nm and a CCD detector (1040 × 258 resolution), and FTIR spectroscopy using PerkinElmer Spectrum Two spectrometer. The Raman spectra were acquired in the spectral range from 250 to 1700 cm^{-1}. FTIR spectra were acquired in the range between 750 and 3700 cm^{-1} using Diamond UATR accessory, the number of scans was 16 and spectral resolution was 4 cm^{-1}. Three measurement points were defined for each of the tested specimens: C-point was defined in the ~~area~~ centre of a damage, N-point was defined 5 mm from C-point, and F-point was defined 30 mm further. The choice of measurement points allowed for analyzing and comparing the induced changes of chemical structure of composite material in (C-point) and close to (N-point) the place of the highest intensity of mechanical fatigue, i.e. the region of stress concentration, where the specimens reached the highest temperature due to the self-heating. Additionally, the effect of self-heating phenomenon was measured for the part of a composite that was located in a certain distance from the C-point in which almost no increase in temperature was observed (F-point). The morphology of specimens was measured in the same defined C, N and F-points by means of scanning electron microscope Phenom Pro-X equipped with 3D Roughness Reconstruction software. For the further characterization of the profiles, selected specimens were cut along the line of maximum loading (C point) and the Raman spectra as well as SEM images were collected from the exposed regions.

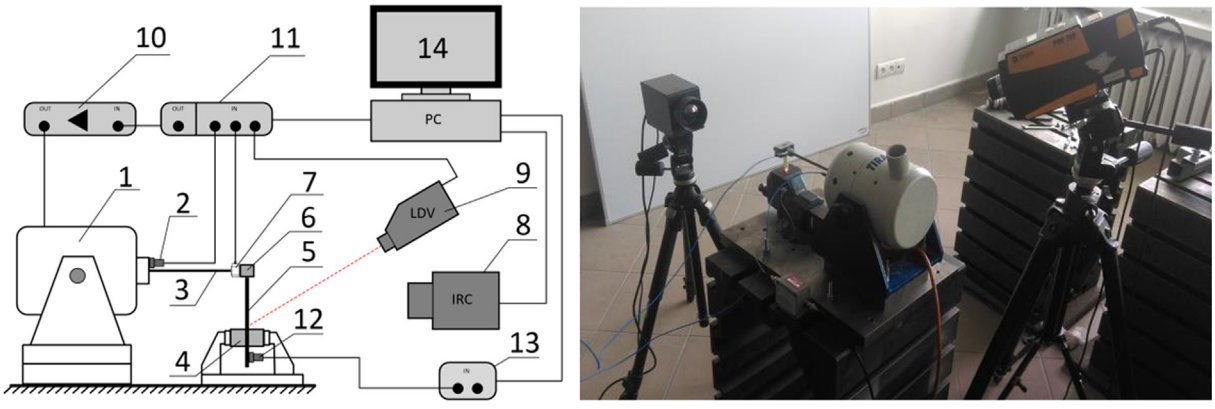

Fig. 1. The scheme and the pictures of the test rig used for fatigue tests.