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Stress corrosion of epoxy-glass composites monitored using acoustic emission

Korozja naprężeniowa w kompozytach epoksydowo-szklanych monitorowana z zastosowaniem emisji akustycznej

Abstract

In the building industry, polymeric matrix composites filled with glass, carbon, graphite, polypropylene, or Kevlar filaments are commonly used. However, it is notable that the wider use of composites is limited by a lack of sound knowledge regarding their properties their responses to exposure to various environments. In this respect, the alkaline and acid environments may have a significant influence on the response of epoxy-glass composites which are most commonly in use. They may undergo stress corrosion and the resulting cracks reduce the strength of the composite. Within this work, a method based on acoustic emission measurement is devised which allows the determination of the beginning of cracking and of the intensity of the corrosive cracking of filaments in a loaded composite. This is substantial in terms of the diagnosing of the functioning structures.

Keywords: monitoring, acoustic emission, stress corrosion, epoxy-glass composites, destructive processes

Streszczenie

W budownictwie najczęściej używane są kompozyty z matrycą polimerową wypełnioną włóknami szklanymi, węglowymi, grafitowymi, polipropylenowymi oraz kevlarowymi. Szersze zastosowanie tych materiałów jest jednak ograniczone ze względu na brak dokładnej wiedzy o ich właściwościach i zachowaniu w różnych warunkach ekspozycji i pod różnym typem obciążenia. W literaturze powszechnie istnieje opinia, że kompozyty włókniste na bazie żywic polimerowych są odporne na działanie środowiska zasadowego i kwasowego, co w przypadku uwzględnienia obciążenia tych kompozytów nie jest prawdą. Kompozyty te w wyniku obciążenia mogą ulegać korozji naprężeniowej lub erozji, co powoduje zmniejszenie ich wytrzymałości, a w konsekwencji pękanie. Stosując metodę emisji akustycznej, istnieje możliwość wykrywania i śledzenia procesów korozyjnych w kompozytach na bazie żywic epoksydowych i włókien szklanych, co jest niezmiernie ważne dla bezpieczeństwa użytkowanych konstrukcji.

Słowa kluczowe: monitoring, emisja akustyczna, korozja naprężeniowa, kompozyty polimerowo-szklane, procesy niszczące

1. Introduction

Composites reinforced with continuous fibres have been used for many years in aviation, the armaments industry and sports equipment manufacturing. Over the last decade, the use of composite materials has grown considerably in the building industry, both as strengthening materials and as self-contained structural elements. This trend has now intensely developed in many countries all over the world [1–6].

In the building industry, composites using a polymeric matrix (epoxy resin, polyester resin, phenol resin) are most commonly filled with glass, carbon, graphite, polypropylene, or Kevlar filaments [7–11]. However, it is noted that the wider use of composites is limited by a lack of sound knowledge regarding their properties and their responses to exposure to various environments [9, 11–13].

In general, the selection of an adequate set of characteristics of a composite depends on the prevailing operating conditions and strength requirements. Consequently, it is considered to be of major practical importance to obtain knowledge on the long term performance of composites under a continuous mechanical load exposed to an aggressive environment [5–9].

In the above context, alkaline and acid environments may have a significant influence on the response of epoxy-glass composites which are most commonly in use. They may undergo stress corrosion and the resulting cracks would reduce the strength of the composite [13–17]. Insufficient information about the stress corrosion of such fibres in various chemically active environments is an obstacle to the widespread use of glass fibre composites in the building industry [17–20].

Because of the use of composites in construction, mechanical properties which predominantly depend upon the type and quantities of fibres, the manner of reinforcement, the type and properties of the matrix, the methods of formation and the conditions of hardening are the most important [21–25]. The Young's modules of organic composites with glass fibres is not very high due to the low rigidity of both fibres and resins. In each type of reinforcement, the strength can change depending upon the relative volumetric quantity of fibres.

Because of the following uses of composite materials, it is quite important to know whether or not their volume is substantially changed as a result of stress corrosion. [2–6, 12, 17]:

- as new structural elements;
- in the repairing of elements damaged during use;
- in reinforced elements of building structures the load capacity of which should be increased due to larger loads at exploitation.

This knowledge is especially important because in the materials commercially available, there is always a fibre content threshold, above which the strength drops because of an excessive amount of pores, the bond between the fibres and the matrix being too weak, the non-wetting of some fibres, and other technological defects. The degree of defectiveness of a product is most dependent upon the methods of formation; therefore, for each type of reinforcement, different strengths of products may be obtained.

In composites reinforced one-directionally, their tensile strength mostly depends on the fibres, while bending strength, crushing strength, shear strength and crack resistance of composites of various types of reinforcement predominantly depends upon properties of the resins [2, 4–6].

2. The impact of tensile corrosion on the change of the susceptibility of epoxy-glass composites

Results of microscopic observation (performed by the authors) of the corrosive cracking of a polymeric composite reinforced with parallel laid glass fibres under uniaxial tension in a solution of calcium hydroxide $Ca(OH)_2$ with pH ranging from 8 to 12 and in regular hydrochloric acid HCl are presented in Figs. 1–5.

A high load causes cracking of the matrix (perpendicular to the direction of the reinforcement), which consequently eases penetration of the corrosive solution into the composite (Fig. 1), or the crushing of the resin and the exposing of the surface of the fibres. Both phenomena cause a loss of protection of the fibres provided by the matrix. As part of this research, a method was worked out allowing for the determination of the beginning of cracking and the intensity of corrosive cracking of filaments in a loaded composite [17]. This is substantial in terms of the diagnosis of the functioning structures.

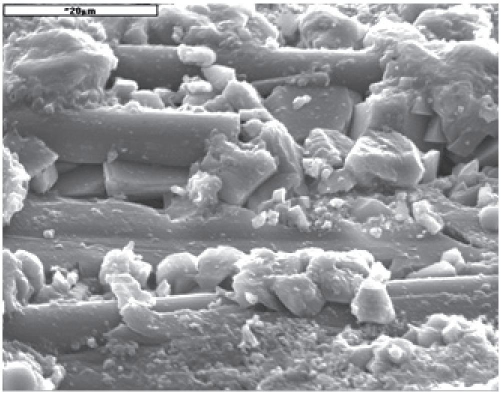

Fig. 1. Cracks of the resin due to high load

As more and more fibres get exposed due to the breaking of the matrix, a process of the penetration of a corrosive environment into the material begins – this leads to the expansion of cracking perpendicular to the reinforcement (Fig. 2), thus breaking its continuity.

As a result of the penetration of an alkali into the cross-section of a composite, the fibres which form reinforcement undergo a gradual degradation and ultimately break due to stress corrosion [16]. Fig. 3 presents the surface of a crack of a composite resulting from load and the concentration of $Ca(OH)_2$ at about pH12 in the composite (glass fibres – epoxy resin).

Sedimentation which appears on the surface of broken fibres, as mentioned before, is probably the product of the reaction of the alkali with the silicon contained in the fibres.

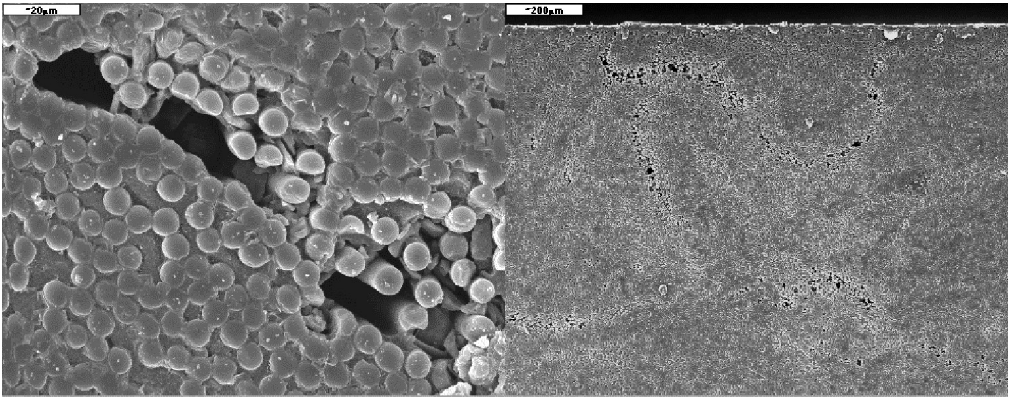

Fig. 2. The depth cracks resulting from further penetration of the solution into a composite

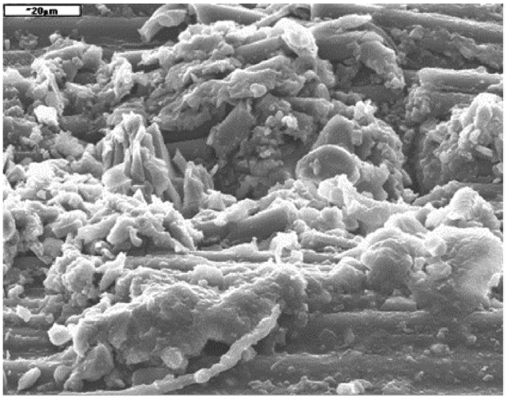

Fig. 3. Surface of composite cracks

The magnified element with oblique cracks shows that there are pits which appeared as a result of the corrosion of fibres and of the breaking of the resin. These pits form extensive and deep cavities on the surface of the reinforcement, corresponding with the manner of destruction of individual fibres as discussed above.

The degree of concentration of the solution and the load level can either speed up or slow down the process of corrosive cracking.

The image across the surface of the tested composite (Fig. 4) shows that the hydrochloric acid (HCl) caused the occurrence of a large number of corrosion pits on the surface of the fibres; furthermore, separation between the fibres and the matrix is visible – this enables penetration of the solution into the composite. The superficial corrosion of fibres occurs most commonly where the matrix and the fibres are joined. In the place where the resin is cracked, hydrochloric acid HCl causes the occurrence of substantial cavities on the surface of the fibres.

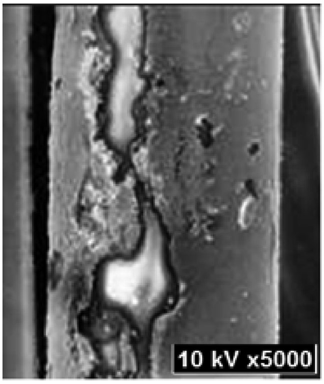

Fig. 4. Magnified section of fibres with corrosion damage

As has been observed, three damage mechanisms can occur during the corrosion:
- cracking of the resin;
- degradation of fibres;
- breaking of fibres.

Although the damage process can be observed microscopically, this can only be achieved in a laboratory environment; therefore, for the in situ testing of real structural elements, it is necessary to use other methods that are non-destructive in order to detect such processes.

In this paper, the acoustic emission (AE) method was applied to detect for the presence of corrosion stress.

3. Identification of AE signals generating during the corrosive cracking of an epoxy-glass composite

3.1. Preliminary tests results

The static test was carried out using the tensile testing machine presented in Fig. 5.

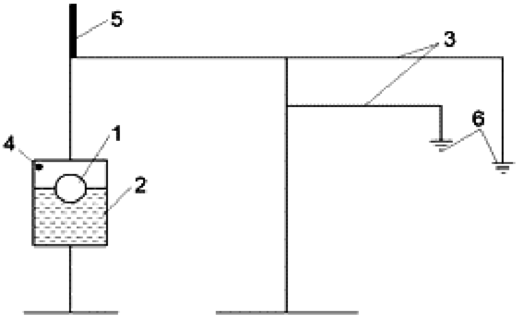

Fig. 5. Scheme of a tensile testing machine

It consists of a set of levers (3) of leverage x10 and x30, and a sample type NOL [26, 27] (1) immersed in a vessel containing solution $Ca(OH)_2$ (2). On the surface of the sample a, broad-band sensor of acoustic emission (4) was secured, and a 'Peltron' sensor (5) was placed at the beginning of the lever arm to measure the elongation. The whole system was loaded with a set of weights (6).

Samples was ring-shaped with an internal diameter of 42.25 mm and a wall thickness of 5.5 mm with the share of fibres by volume $V_1 = 0.50$. The mean force destroying the composite was identified as $P_n = 10$ kN.

The Young's modulus for the sample was found to be $E_1 = 37$ GPa.

Preliminary acoustic tests were carried out for two levels of load equal to 0.5 and 0.7 of P_n for two concentrations of solution $Ca(OH)_2$ – pH8 and pH12 – the results of these tests are presented in Figs. 6 & 7, where 'Δl' marks the displacement line and 'EA' marks the line showing the sum of acoustic events.

A sudden increase in the sum of events during the process of loading, accompanying the growth of displacement, is connected with the breaking of individual fibres of the composite and the growth of tensions in the tested sample. The diagrams show that the change of susceptibility is in this case, a discrete process and it occurs jerkily; this is characteristic of brittle materials.

If a change of elongation occurs in a steady manner, then the signal AE does not increase rapidly. It is observed that increases in both emission and displacement are connected.

It is seen that at 0.5 P_n, in the first stage of work of the composite, bearing the initial load, the growths of both signals and of displacement are continuous and linear. During the immersion in the solution, the process begins to progress in a jerky manner, although this is not particularly intense.

At a load level of 0.7 P_n, it appears that the process of growth of both displacement and AE is non-linear and non-continuous, and changes of recorded parameters are clearly visible.

It can be observed that by analysing the signal of acoustic emission, it is possible to assess the intensity of development of defects in composites as a result of the simultaneous influence of tension and a corrosive environment. Hence, the establishment of a special experimental program.

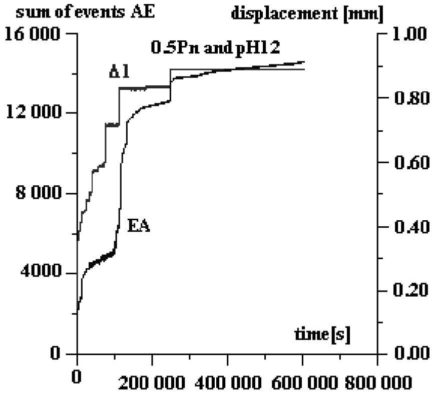

Fig. 6. The results of initial acoustic tests for load of 0.5 P_n and solution of $Ca(OH)_2$ at pH 12

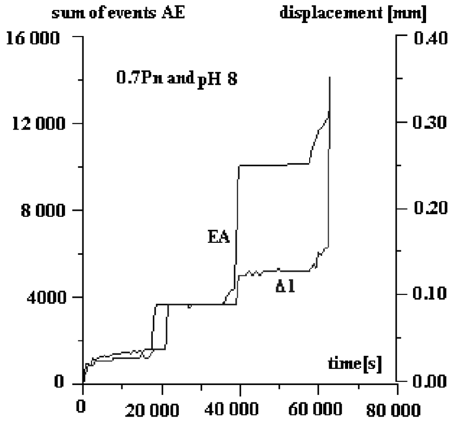

Fig. 7. The results of initial acoustic tests for load of 0.7 P_n and solution of $Ca(OH)_2$ at pH 8

3.2. Experimental results

Experiments were performed on an epoxy-glass composite subjected to three-point bending in an alkaline environment. The test was carried out for constant displacement.

Polymeric composite bars reinforced with parallel running glass fibre in a solution of $Ca(OH)_2$ and 3% NaCl of varying concentrations ranging from pH8 to pH12 – for reference purposes, testing was also carried out in normal hydrochloric acid (HCl). The composite bars had a matrix of epoxy resin and fibres of type ER-3005, the share of the fibre by volume was $V_f = 0.72$. The fibres were made of glass E (boro-alumino-silicate) containing under 1% of alkalis, with a tex value of 1200 g/km and nominal diameter of the elementary filament Ø = 10 μm, it was manufactured by Krosno Glassworks. The choice of both of the environment and the concentration of them results from the assumed conditions of operation of the strengthening concrete elements. The concentration of pH12 corresponds to the surface of non-corroded concrete, while pH8 to the surface of corroded concrete.

The tapes with dimensions 200 × 6 × 3.2 mm were tested under simultaneous influence of corrosive environment and force as it is shown in Fig. 8.

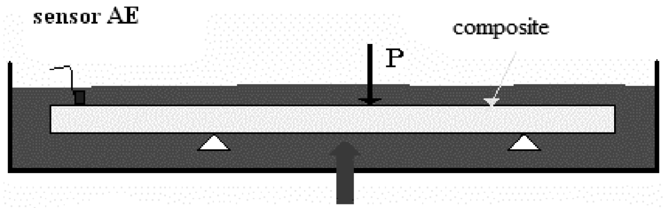

Fig. 8. Scheme of tests of composite bars

The process of corrosive cracking was recorded by a 'MISTRAS 2001' acoustic emission processor; acoustic emission signals were measured using broadband sensors of frequencies from 100 to 1000 kHz and a resonance sensor of 55 kHz frequency. The measurements were carried out with the use of an amplitude filter in the range of 40 to 100 dB. The obtained signals were subjected to a Fourier transformation. At the same time, in order to assess the change of susceptibility of the tested samples, it was measured their elongation in the function of time under constant load. The measurement was made by 'PELTRON' sensors with a measurement range of 0 to 1 mm. The whole test was recorded in a computer using an analogous-digital card.

During the test, such AE parameters as the sum of events, amplitude, duration and rise time in the function of time were recorded. Additionally, the AE waveform and wave spectrum were analysed.

Three types of waves occurring in sequence in the process of corrosive cracking in an alkaline environment $Ca(OH)_2$ can be distinguished (Fig. 9–11).

Signals of type 'a' are the most common and include around 90% of all recorded acoustic signals; they are characterised by their short rise time and short duration. The spectrum of the signal does not exceed 1 MHz, and the amplitude is in the region of 45 dB. The signal reaches its highest value in the range of 200 to 250 kHz. It is assumed that such a signal is due to the breaking of the epoxy matrix of the composite.

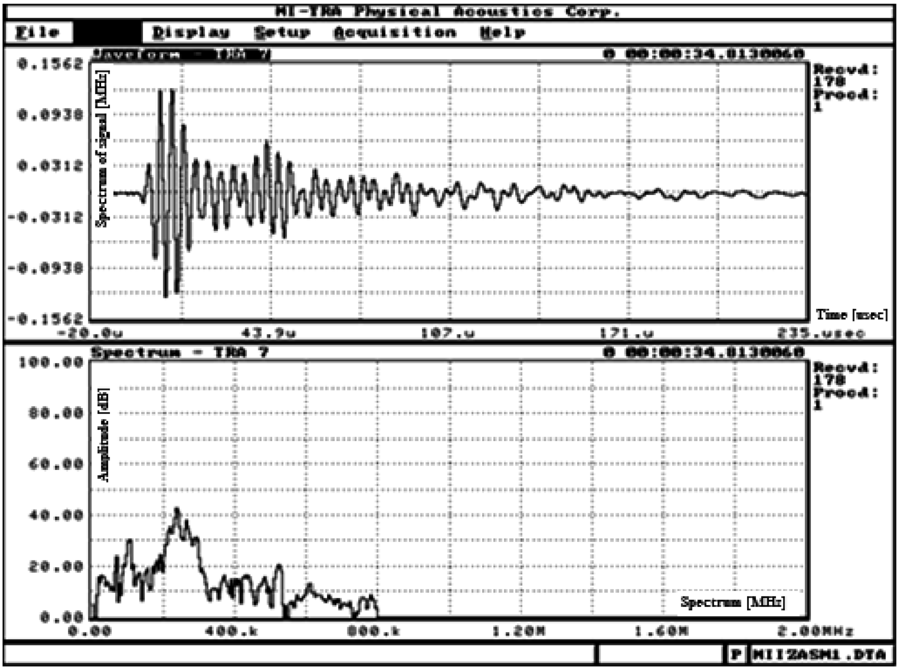

Fig. 9. The emission signal of type 'a'

A second type, signal 'b', is characterised by a higher amplitude reaching a level of 60dB and the spectrum of up to 1.2 MHz; it has a longer rise time and duration than type 'a' – this is probably due to the breaking of the fibres of the composite reinforcement as a result of corrosion– its spectrum does not drop linearly but has local peaks. Corrosion in an alkaline environment does not occur rapidly, this is probably why the amplitude of the signal is so low. This type of signal accounts for around 5% of the registered signals.

The last 5% belong to the acoustic signal of type ‘c’ – this substantially differs from the two previous types of signal; it is characterised by a short rise time and long duration. The spectrum shows that the amplitude of the signals exceeds 60 dB and that they fill the entire spectrum. It can also be noticed that the signal reaches its maximum value in the range of 250–300 kHz. It is assumed that this type of signal occurs due to the breaking of fibres. This means that in the case of an alkaline environment, three damage mechanisms due to load corrosion observed microscopically can also be identified using the analysis of the acoustic emission signal. This means that in the case of an alkaline environment, three damage mechanisms due to load corrosion observed microscopically can also be identified using the analysis of the acoustic emission signal.

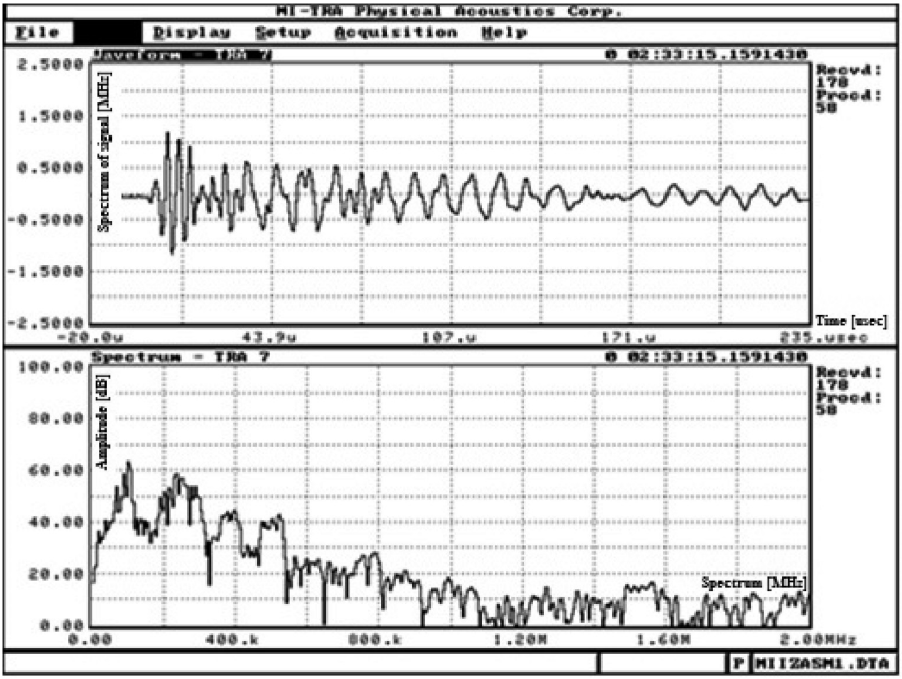

Fig. 10. The emission signal of type ‘b’

The situation is not the same if the epoxy-glass composite is immersed in normal hydrochloric acid HCl. As a result of measurements of signals of acoustic emission in the process of the loading of a composite in acid, two types of signal were identified which appeared in the course of the experiment (Fig. 12, 13).

Signals of type ‘d’ are characterised by their low energy and short rise time, its spectrum is confined within the range of 100 kHz to 1 MHz, and the amplitude does not exceed a value of 45 dB. In the measurement file, signals of this type account for around 95%. It is similar to signal ‘a’ and is assumed to be due to the breaking of the epoxy matrix of the composite.

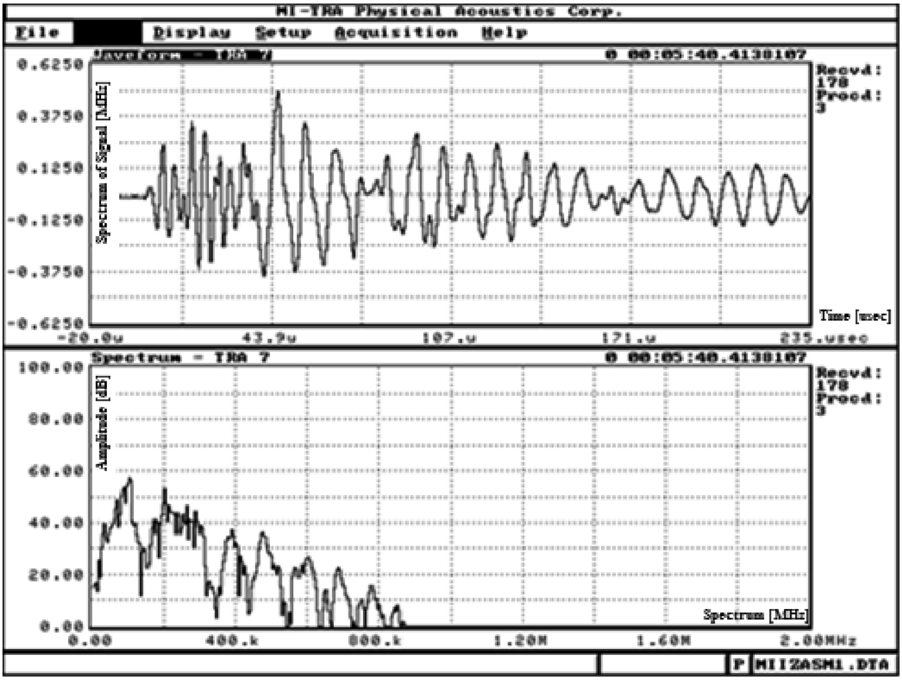

Fig. 11. The emission signal of type 'c'

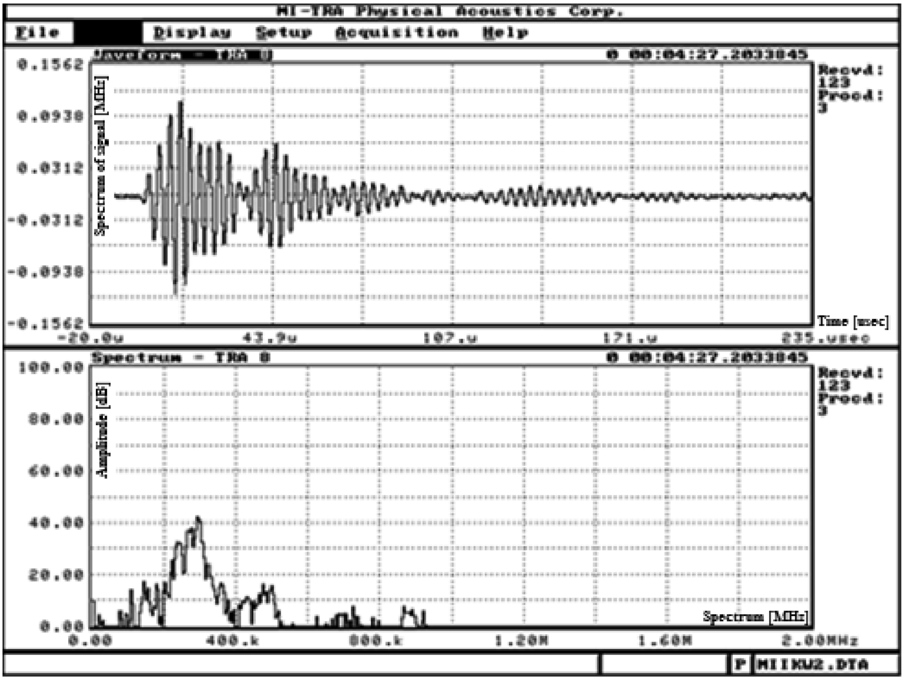

Fig. 12. The emission signal of type 'd'

Signals of type 'e' make only around 5%. They have very high energy, a short rise time and a short duration. They include the full spectrum in the range of 100 kHz to 2 MHz. Under such a load, stress corrosion ran quickly and rapidly [16]. It is assumed that the obtained type of signal is due to two mechanisms: fibre degradation and breaking of fibres resulting from the influence of the acid and the high load. Its peak, as with the case of breaking due to corrosion, occurred in the range of 250–300 kHz.

In the case of the acid environment, damage mechanisms occurring as a result of load corrosion observed microscopically can be identified using the analysis of the acoustic emission signal.

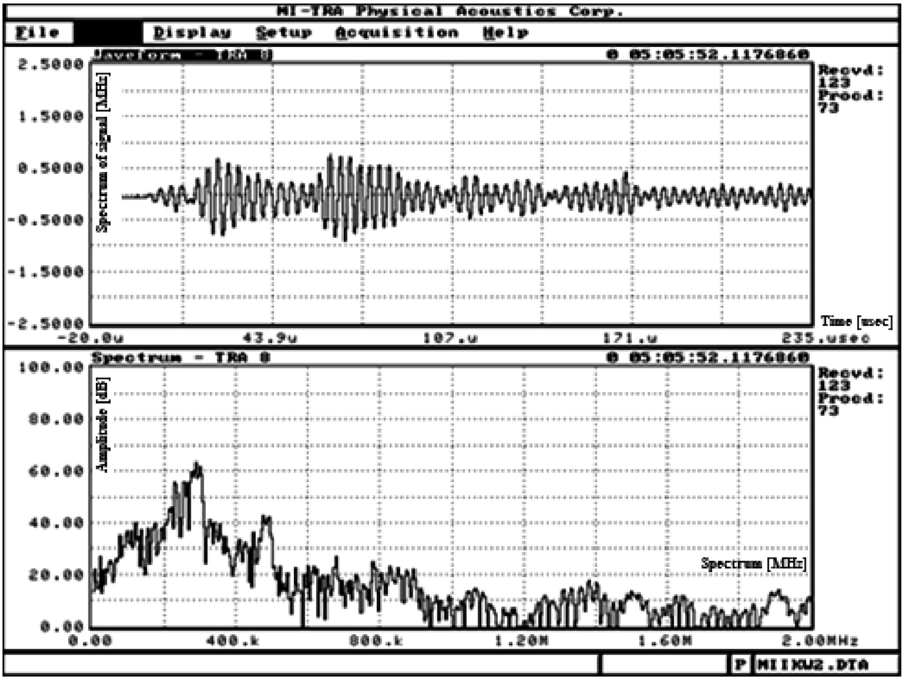

Fig. 13. The emission signal of type 'e'

4. Conclusions and final remarks

On the basis of the obtained results and an analysis thereof, the following conclusions can be formulated:

- cracking of the reinforcement of a composite due to corrosion is influenced both by acidic and alkaline environments;
- specific types of acoustic signals can be assigned to different mechanisms of cracking;
- using the acoustic emission method, different cracking mechanisms can be identified;
- it is possible to detect the intensity of the cracking process;
- full usefulness of the method of acoustic emission to determine the beginning of cracking due to corrosion has been proven, as has its usefulness in following the development of cracks which cause destruction of the reinforcement of a composite,

- the process of destruction due to corrosion occurs fastest in an alkaline environment of concentration pH8 – pits occur which go deeply into the structure of the fibre, these probably cause the leaching out of ions Ca2+, Mg2+ and Na+,
- no corrosion was noticed in a non-loaded bunch of fibres exposed to a long-lasting influence of an alkaline environment $Ca(OH)_2$ – this reflects a strong influence of load on stress corrosion.

Cracking caused by corrosion is very dangerous in terms of the use of constructions strengthened with a composite because the process is not perceptible without special tests. Corrosion has an important influence on the strengthening elements in two ways:

- the cracking composite increases its susceptibility, thus reducing the strengthening effect;
- as a result of corrosive cracking, the entire composite undergoes destruction.

Therefore, in the case of damage of this nature, the use of acoustic emission is a very helpful technique in determining the degree of degradation of the strengthening element.

An analysis of the obtained results led to the identification of types of signals which characterise the destructive mechanisms which occur during stress corrosion in the entire volume of the test element. Moreover, it was confirmed that acoustic emission is useful for identifying the beginning of cracking as well as for following the process of corrosion of a composite.

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