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ENVIRONMENTAL STRESS CRACKING IN E-GLASS AND ARAMID/GLASS EPOXY COMPOSITES

Glass fibre reinforced polymer composites (GFRP) show relatively low degradation in various corrosive environments in the unstressed state, however, they are very susceptible to stress corrosion, especially in dilute mineral acid environment. The stress corrosion crack propagation characteristics in glass fibre/epoxy laminates have been studied by several investigators. However, there is no relevant data on the behaviour of hybrid aramid-glass fibre polymer laminates (A-GFRP), now employed in construction of special vessels for naval and sport use. Due to high water absorption in aramid/epoxy laminates (5÷6%) hybrid aramid-glass/epoxy composites may be susceptible to early cracking. Accordingly, in the present work environmental stress cracking characteristics of GFRP and (A-G)FRP were studied using CT (fracture mechanics) samples (Fig. 1) under constant tensile load and water environment. For GFRP the characteristics of crack length as a function of exposure time (up to 3 months) were obtained (Fig. 3). The threshold stress intensity factor for environmental crack growth was found K_I = 15 MPa · m$^{1/2}$ in water compared to 22 MPa · m$^{1/2}$ in air (Fig. 4). In hybrid (A-G)FRE composite only surface resin crack was found (Fig. 5) accordingly compared to GFRP (A-G)FRE composite was found practically immune to the environmental stress cracking in the conditions used in this study. Ductile aramid fibres seemed to protect the glass fibre reinforcement from stress cracking due to higher chemical resistance and complex failure mechanisms (Fig. 6).

Keywords: **laminates, polymer composites, environmental stress cracking**

BADANIA PĘKANIA ŚRODOWISKOWEGO LAMINATÓW EPOKSYDOWYCH WZMOCNIONYCH WŁÓKNAMI SZKLANYMI I ARAMIDOWYMI

Kompozyty epoksydowe wzmocnione włóknami szklanymi są dość odporne na wpływy środowiskowe w stanie nieobciążonym, jednak po przyłożeniu obciążeń łatwo pękają w środowisku wody i rozcieńczonych kwasów. Charakterystyki propagacji pęknięć środowiskowych w laminatach szklano/epoksydowych były przedmiotem wielu prac, jednak brak jest danych na temat zachowania laminatów o wzmocnieniu hybrydowym aramidowo-szklanym, stosowanych w budowie kadłubów specjalnych, szybkich jednostek pływających. Ze względu na znaczną absorpcję wody (rzędu 5÷6%) przez kompozyty aramidowe istnieje niebezpieczeństwo przyspieszonego pękania obciążonych elementów z laminatów aramidowo-szklanych w środowisku wody. W niniejszej pracy zbadano zatem przebiegi charakterystyk propagacji pęknięć w próbkach ze szczeliną (mechaniki pękania), CT (rys. 1) z laminatów szklano/epoksydowego i aramidowo-szklano/epoksydowego przy stałym obciążeniu rozciągającym. Dla kompozytu z włóknami szklanymi zanurzonego w wodzie destylowanej otrzymano charakterystyki przyrostu długości pęknięcia w funkcji czasu ekspozycji w wodzie i w powietrzu (rys. 3). W laminacie szklano/epoksydowym progowa wartość współczynnika intensywności naprężeń wyniosła K_I = 15 MPa · m$^{1/2}$ w porówaniu z 22 MPa · m$^{1/2}$ w powietrzu (rys. 4). Dla laminatu hybrydowego wzmocnionego włóknami aramidowymi i szklanymi pęknięcie przebiegało jedynie w powierzchniowej warstwie żywicy (rys. 5), zatem w zastosowanych warunkach i czasach ekspozycji (3 miesiące) nie udało się określić prędkości propagacji pęknięcia. W porówaniu z laminatem wzmocnionym włóknami szklanymi laminat hybrydowy okazał się więc praktycznie odporny na pękanie środowiskowe w zastosowanych warunkach, niezależnie od podwyższonej chłonności wody. Proces pękania włókien szklanych hamowały odporne na pękanie włókna aramidowe splecione ze szklanymi w jedną tkaninę (rys. 6). Zaobserwowano złożony mechanizm degradacji materiału na końcu szczeliny, co opóźniało pękanie na grubości materiału.

Słowa kluczowe: **laminaty, kompozyty polimerowe, pękanie środowiskowe**

INTRODUCTION

Glass fibre reinforced polymer composites (GFRP) are widely used in the marine applications and in chemical industries as pressure vessels, containers, pipes. Although they show relatively low degradation in various corrosive environments in the unstressed state, they are very susceptible to stress corrosion, especially in dilute mineral acid environment [1, 2].

Environmental stress-cracking in GFRP takes place as a result of combination of loads and exposure to a corrosive environment. In particular stress corrosion cracking (SCC) occurs when sharp cracks initiate and propagate through the material as a direct consequence of the weakening of the glass fibres by the acid. The strength of the fibres is reduced dramatically as a result of diffusion of the acid to the crack tip to effect chemical attack of the fibre surface, which causes

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a highly planar fracture with a much reduced failure stress. The toughness and fatigue resistance are also sharply reduced, since the fibres all break in the crack plane and pull out work is virtually zero [3].

Hogg has shown [4] that stress corrosion of GFRP can occur in the absence of prior resin cracking. The acid is postulated to reach the fibers by flowing through microcracks, crazes or voids in the matrix, which occur as a consequence of the stress intensification ahead of the crack tip of a growing stress-corrosion crack. Fibre weakening and the failure process occur sequentially at the tip of a growing crack and there is evidence that the fibres fail in a stepwise pattern (or "river line") with a discrete delay period between individual fibre breakages. The delay period is associated with the time required for the acid to reach the fibre surface and to promote weakening of the fibre, so as to break under the combined action of the local load and the acid [5].

Stress corrosion cracking is characterized by the formation of a planar crack which usually grows at right angles to the principal fibre direction, be it through unidirectional, cross-ply or random fibre composites. The rate of growth depends on the applied stress and the environment. Consequently the lifetime of a component or structure made from GFRP subjected to stress corrosion conditions can be predicted, provided the dependence of crack growth rate on stress intensity at the crack tip is known [4].

The development of environmental stress cracking depends not only on the composition of the glass fibres, but also on the fibre architecture and other factors which govern the environmental resistance of fibrous polymer laminates. The majority of results on environmental stress cracking in GFRP refer to unidirectional fibre reinforced composites, however the author studied environmental stress cracking of woven fibre fabric reinforced laminates of both glass and aramid-glass/ epoxy laminates now employed in construction of special vessels for naval and sport use.

EXPERIMENTS AND RESULTS

Laminates were fabricated from woven orthogonal balanced fibre fabrics: E glass (STR 66-110, Krosno, Poland) and intermixed aramid-glass fibre fabric (REA 390S) (SP Systems, UK). Standard pro-adhesive treatment of the fibres for use with epoxy resins was provided by the suppliers. Laminates consisted of 10 plies of fabric impregnated with epoxy resin by hand lay-up. The resin was Epidian 52 (Organica-Sarzyna), typical Diglycidyl Ether of Bisphenol - A (DGEBA) cured with amine hardener ET (20 wt.%). The approximate fibre volume fraction was $V_f = 40\%$.

The thickness was $t = 4.2$ mm. The tests were performed on the compact-tension (fracture mechanics-CT) specimens (Fig. 1). Samples were immersed in water under constant load. Pre-crack (2 mm) was made using a sharp blade and its further 0.5 mm sharp extension was produced by cyclic loading.

Figure 2 shows the test machine for constant loading under water environment. The crack length was measured using a travelling microscope. The measurements were stopped when deviation from normal direction occurred. The rate of crack propagation was assessed on the basis of crack growth time (Fig. 3).

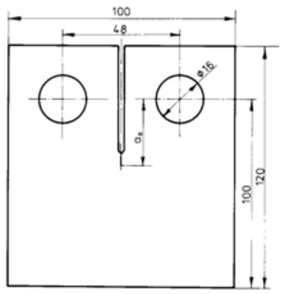


Fig. 1. Geometry of the CT specimen

Rys. 1. Geometria próbki CT

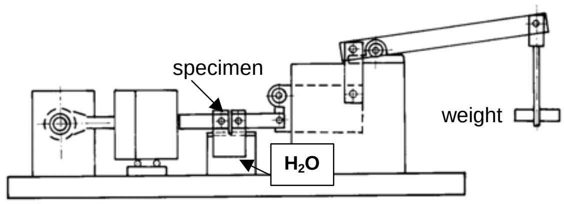


Fig. 2. Machine for measuring crack growth rate under constant loading in water or acid environment

Rys. 2. Stanowisko do badania propagacji pęknięć środowiskowych przy stałym obciążeniu

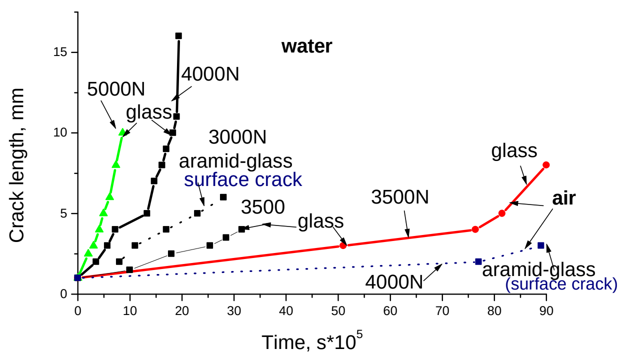


Fig. 3. Crack length as a function of exposure time in water

Rys. 3. Wykresy przyrostu długości pęknięć funkcji czasu ekspozycji w wodzie

The stress intensity factor was calculated using the equation

$$K_I = \frac{P}{t\sqrt{w}} F\left(\frac{a}{w}\right) \tag{1}$$

where:

$$F(a/w) = 13.74\,[1 - 3{,}38\,(a/w) + 5{,}57\,(a/w)^2] \quad (2)$$

P - constant load, a - crack length, t - CT specimen thickness, w - the width of the specimen.

Typical curves showing variation of crack length with time for exposure in water for varying loading are illustrated in Figure 3. Two distinct crack growth rate regimes were found: stable crack growth, for exposure times from two-to-three weeks to two-to-three months (depending on the load), and unstable crack propagation, preceded by accelerated growth for several hours. For comparison, the results of tests performed in air are also shown. At 3500 N the initial crack rate in water is almost equal to that in air at the same loading. The delay period is associated with the time required for water to reach the fibre surface and to promote weakening of the resin and the fibres, so as to break under the combined action of the local load and the water. The significant increase in crack growth rate is evident at higher loads, 4000 and 5000 N, resulting in higher crack tip opening displacement and immediate penetration of water to the fibre/matrix interface through matrix cracks. The crack emanating from the notch was normal to the load and the fracture surface was initially flat, with some roughness observable in the SEM. The overall roughness of the fracture surface increased with increasing crack length [10].

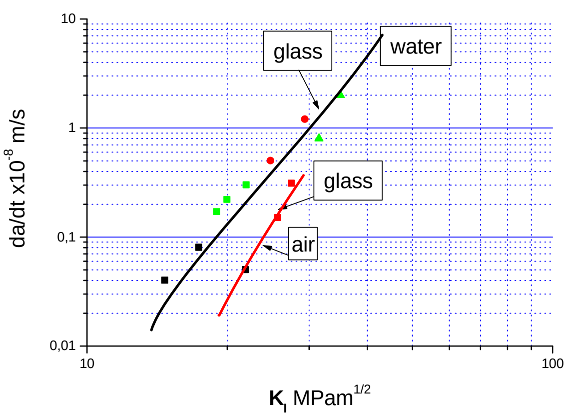


Fig. 4. Crack propagation rate versus stress intensity factor K_I in GFRP

Rys. 4. Prędkość rozwoju pęknięć w funkcji współczynnika intensywności naprężeń K_I dla laminatu wzmocnionego włóknem szklanym

Figure 5 shows the cracks which have grown from the root of the notch in GFRP (a) and (A-G)FRP (b) samples. Apart from some small steps, crack growth is planar over the distance of 5÷6 mm. In the GFRP sample the crack is wide open due to fracture of the transverse fibre strands; however some proportion of the innermost transversely oriented fibres were not affected by the water and remain undamaged or partly pulled out from the matrix (arrow in Fig. 5a). It was observed that in the failure process fibre and interface weakening occur sequentially at the tip of a growing crack.

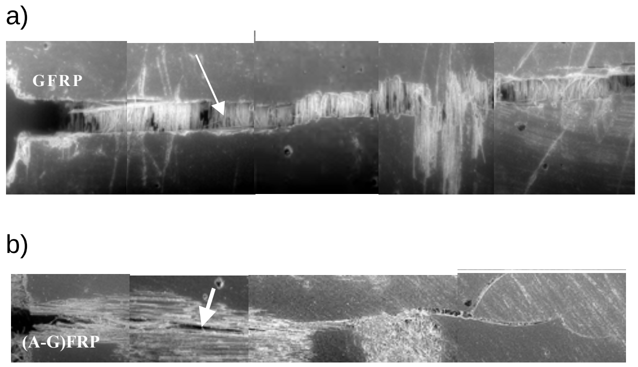


Fig. 5. Crack which has grown from the root of the notch in glass and aramid/glass (a) fibre reinforced epoxy composites (b)

Rys. 5. Pęknięcie rozchodzące się od dna karbu w laminacie wzmocnionym włóknem szklanym (a), aramidowo-szklanym (b)

DISCUSSION

The environmental effect on the fibres was found to be rather small despite some evidence of stress corrosion cracking; the water exposure was not long enough. Accordingly, many features associated with fracture in air or short term water conditioning, such as debonding and fibre pull-out are present.

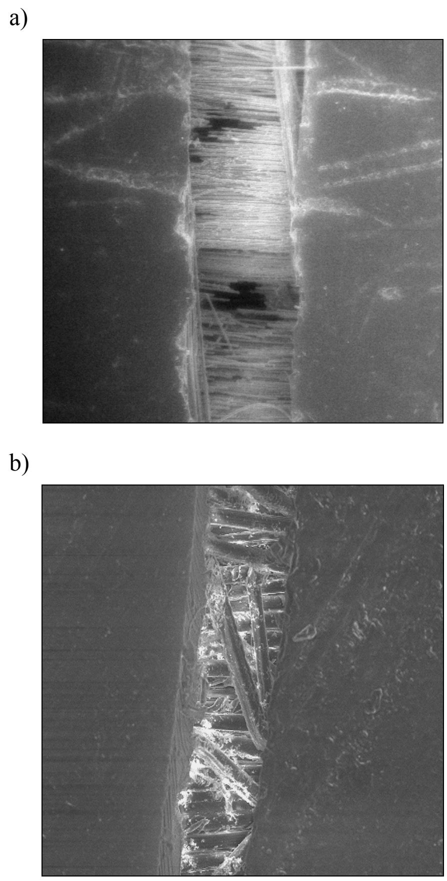
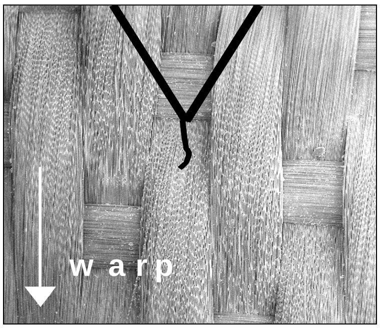


Fig. 6. Through-the thickness crack in GFRP (a), surface resin crack in (A-GFRP) revealing minor damage in the fibrous structure of the laminate (b)

Fig. 6. Pęknięcie na wskroś grubości próbki w laminacie wzmocnionym włóknami szklanymi (a), aramidowymi i szklanymi (b): powierzchniowe pęknięcie żywicy odkrywające niewielkie zniszczenia w strukturze włóknistej laminatu

a)



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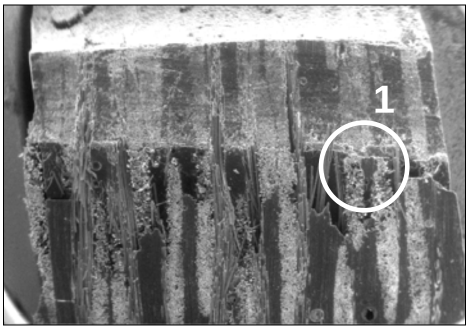
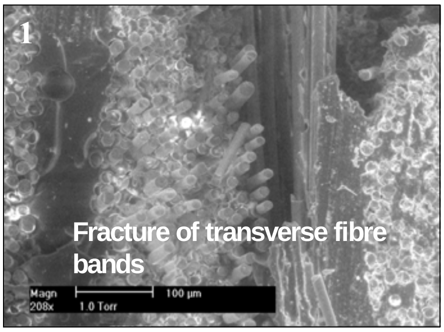


c)



d)

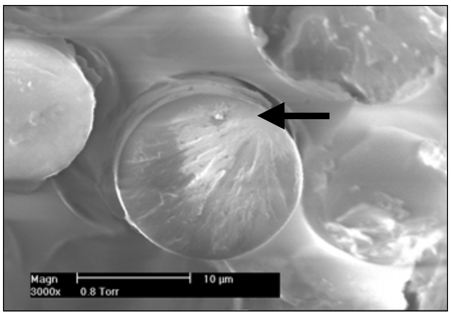


Fig. 7. Schematics of the initial crack orientation with respect to the fibre fabric weave (a), section of GFRP sample in through-the-thickness direction (b): initial crack at the notch root, (c, d) details of Fig. b (circle 1): fracture of transverse fibre bands (c), typical features of stress corrosion cracking of glass fibres: mirror zone (arrow) and river pattern

Rys. 7. Schematyczne przedstawienie orientacji pęknięcia początkowego względem splotu tkaniny z włókien (a), przekrój próbki laminatu szklanego w kierunku grubości (b): początkowe pęknięcie na dnie karbu (c, d), szczegóły rys. b (obszar 1): pęknięte pasmo poprzeczne włókien szklanych (c), typowe cechy kruchego przełomu w wyniku korozji naprężeniowej włókien szklanych: strefa lustrzana (strzałka), wzór dorzeczy

Figures 7a, b show initial crack at the notch root in through-the-thickness direction with typical features of stress corrosion cracking of glass fibres with two stage crack propagation: mirror zone - very smooth nucleation region, corresponding to the slow crack growth due to environmental effects on the glass fibres, and river pattern zone typical of brittle crack propagation (Fig. 7c, d). It has been reported that such features are typical of stress corrosion cracking at high values of stress intensity factor. The lower the stress intensity, the larger the mirror zone on glass fibre fractures. In the author's work, at high stresses, brittle cracking of the resin and fibres occurred before nucleation of significant mirror zone failure. Larger mirror zones were found on the fracture surfaces of glass fibres at the notch root and near the specimen surface, because of their longer and more intensive contact with water.

Hybrid (A-G)FRP appear to be largely immune to environmental stress cracking due to complex failure mechanisms resulting in long exposure times needed for total sample failure. As shown in Figure 6 environmental cracking of (A-G)FRP is a complex process with surface resin cracking followed by interfacial cracking due to aramid and glass fibre debonding, resulting in glass fibre splitting in the surface layer (Figs 5, 6). In this work the tests were interrupted before the crack penetrated the whole specimen thickness, since very long term conditioning was required. Accordingly at this stage values of crack growth rate da/dt were not found, whereas in GFRP specimen through-the-thickness fracture occurred at similar stress intensity as in hybrid (A-G)FRP.

The results of the crack propagation tests on glass fibre reinforced laminates obtained by the author can be compared with those of H. Kawakada et al. [6] for GFRP. Their threshold stress intensity factor was 8 MPa $\cdot$ $m^{1/2}$ in water and 11 MPa $\cdot$ $m^{1/2}$ in air, compared to 15 and 22 MPa $\cdot$ $m^{1/2}$, respectively, obtained in the author's work. Although both composites had similar thicknesses and were made from woven orthogonal glass fabrics by hand lay-up, their fibre volume fraction was as low as 32% and thus the strength of the material was low, which accounts for the difference in the results.

CONCLUSIONS

- For GFRP the threshold stress intensity factor for environmental crack growth was found K_I = = 15 MPa $\cdot$ $m^{1/2}$ in water compared to 22 MPa $\cdot$ $m^{1/2}$ in air whereas hybrid (A-G)FRP composite was found practically immune to the environmental stress cracking in the conditions used in this study due to higher corrosion resistance of aramid fibres which prevented fibre fracture and resulted in complex failure mechanisms.

- In order to propose precise technological solutions to problems associated with marine environments, further studies are needed for large samples of real composites structures.

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Recenzent
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