ENVIRONMENTAL EFFECTS ON THE MECHANICAL PROPERTIES OF PLAIN WEFT KNITTED CF/PEEK AND GF/PET COMPOSITES

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SUMMARY: The effects of hygrothermal exposure on the mechanical properties of knitted fabric reinforced composites (KFRCs) was investigated with respect to their environments in potential applications. Knitted CF reinforced PEEK was immersed in water and simulated body fluid (SBF) at 37, 60 and 90°C for exposure times up to 50 weeks, whereas knitted GF/PET was immersed in water at 90°C for a maximum of two weeks. While no significant effects of long-term exposure on flexural properties, out-of-plane fracture toughness and failure behavior of CF/PEEK were determined, a severe reduction of matrix and fiber/matrix interface properties was observed in GF/PET. Matrix embrittlement and low interfacial adhesion dominated the failure behavior, studied in 4-pt bending and push-out tests. Results suggest that knitted CF reinforced PEEK is highly appropriate for load bearing implants, whereas the application of GF/PET composites is critical in environments involving moisture and elevated service temperatures.

KEYWORDS: Environmental Effects, Thermoplastics, Textiles, Knitted Fabric Reinforced Composites (KFRCs), Interface Degradation, CF/PEEK, GF/PET

INTRODUCTION

Knitted fabric reinforced composites are textile structural composites which offer several adavantages over other composites materials, e.g. excellent drapability and low production costs [1-5]. Knitted carbon fiber (CF) reinforced poly (ether-ether-ketone) (PEEK) is considered for biomedical and aeronautical applications because of its high mechanical properties, its excellent chemical and thermal stability and its superior biocompatibility [6, 7]. Mass production and cost limiting aspects promote the potential of knitted glass fiber (GF) reinforced poly(ethylene-terphtalate) (PET) in the automotive industry.

Even though CF/PEEK is known for high thermal and chemical stability, significant effects of hygrothermal exposure on the mechanical properties of CF/PEEK composites are reported in literature [8-10]. In the presented work, the environmental stability of CF/PEEK knits was investigated with respect to biomaterial applications. Longterm exposure to simulated body fluid (SBF) at 37, 60 and 90°C was investigated. Exposure for up to 50 weeks at 90°C was performed in order to accelerate potential effects of SBF on CF/PEEK since certain implants, e.g. hip joint prostheses, are intended to remain in the body environment over several decades.

The hygrothermal stability of GF/PET is restricted because of its sensitivity to hydrolytic degradation occuring at elevated temperatures. This degradation is related to the decomposing ester groups, leading to decreasing molecular weight, decreasing strength and embrittlement of the PET matrix [11]. In the presented work, knitted GF/PET composites were short-term exposed to H_2O at 90°C to study extend of matrix and fiber/matrix interface degradation and its effect on the macromechanical properties of KFRCs.

MATERIALS AND METHODS

Composite manufacturing:
PEEK yarn, (33 tex, PEEK M, Hoechst, Germany) and CF yarns (3K, 200 tex, HTA5131, Tenax, Germany) were coknitted using the contrary circular knitting technique [12], at a yarn ratio of 4 (PEEK) / 1 (CF), i.e. 52.5% fiber volume content. Commingled GF/PET yarn was obtained from Vetrotex, France. The fiber volume content of the yarn was 50% at a linear density of 730 tex. Circular, low areal density plain weft knits made from CF/PEEK and GF/PET yarns were consolidated in a hot press to flat panels at 420 °C, 30 bar for 30 min and at 290 °C, 20 bar for 20 min, respectively. The panels consisted of 6 and 4 stacked double layers of knitted fabric for CF/PEEK and GF/PET, respectively. Structure and structural units of a single weft-knitted fabric are presented in Fig. 1.

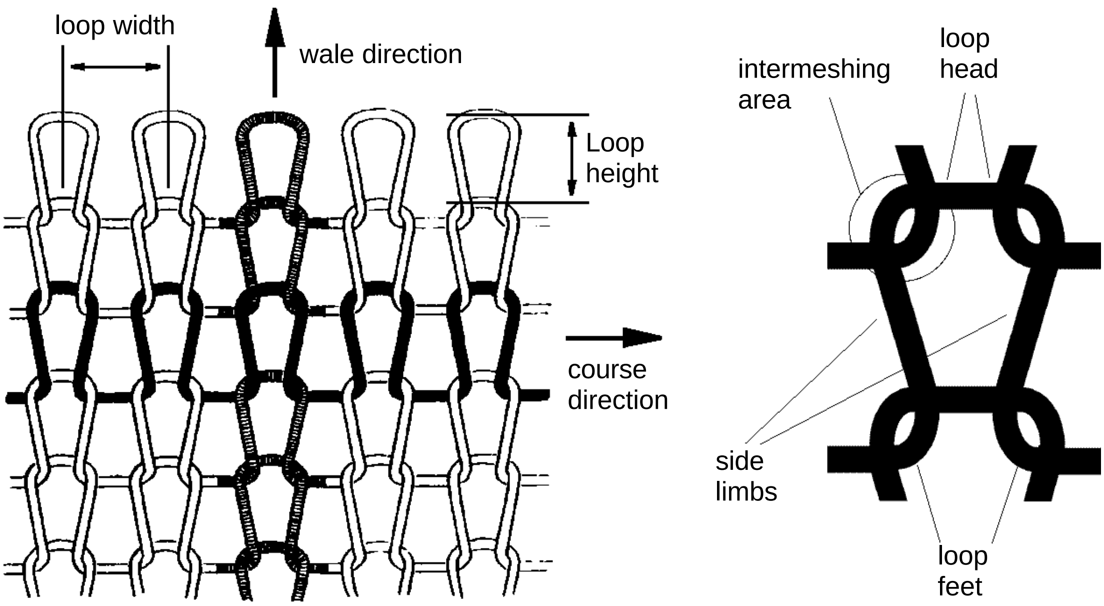

Fig. 1 Structure of plain weft-knitted fabrics. Knitted fabric reinforced composites exhibiting large loops (areal loop density = 2.6 loops/cm$_2$) were studied in the presented work. Loop height / loop width was 7.5 mm / 4.5 mm and 5.4 mm / 7.5 mm for CF/PEEK and GF/PET, respectively.

Environmental conditions:
CF/PEEK and GF/PET samples were fully immersed in H_2O at 90°. Maximum exposure time was 50 and 2 weeks for CF/PEEK and GF/PET, respectively. With regard to the biomedical potential of CF/PEEK, the influence of a hydrous solution with physiological concentratin of mineral components (simulated body fluid, SBF) at different temperatures (37, 60, 90°C) was investigated.

Characterization:
Four-point (4-pt) bending strength and modulus in wale direction (Fig. 1) was determined according to to ASTM D 790M. Fracture toughness K_{IC} of knitted CF fiber reinforced PEEK was assessed by means of compact tension testing and linear fracture mechanics. A detailled description of this procedure is given in [13]. Interface properties of knitted glass fiber reinforced PET were studied by means of the push-out method, as described in [14]. Fracture surfaces, resulting from micro- (push-out) and macroscopical tests (4-pt bending, compact tension) were investigated using SEM.

RESULTS

Knitted CF reinforced PEEK:
Long-term exposure of CF/PEEK knits caused no detectable changes, neither in mechanical properties (Fig. 2) nor in fracture surface morphology (Fig. 3). All variations in fracture toughness K_{IC}, bending modulus and strength remained within standard deviations after exposure to SBF and H_2O at 90°C for up to 50 weeks. The fracture surfaces exhibited short pull-out lengths before and after exposure, suggesting that interface strength was not reduced significantly by environmental degradation.

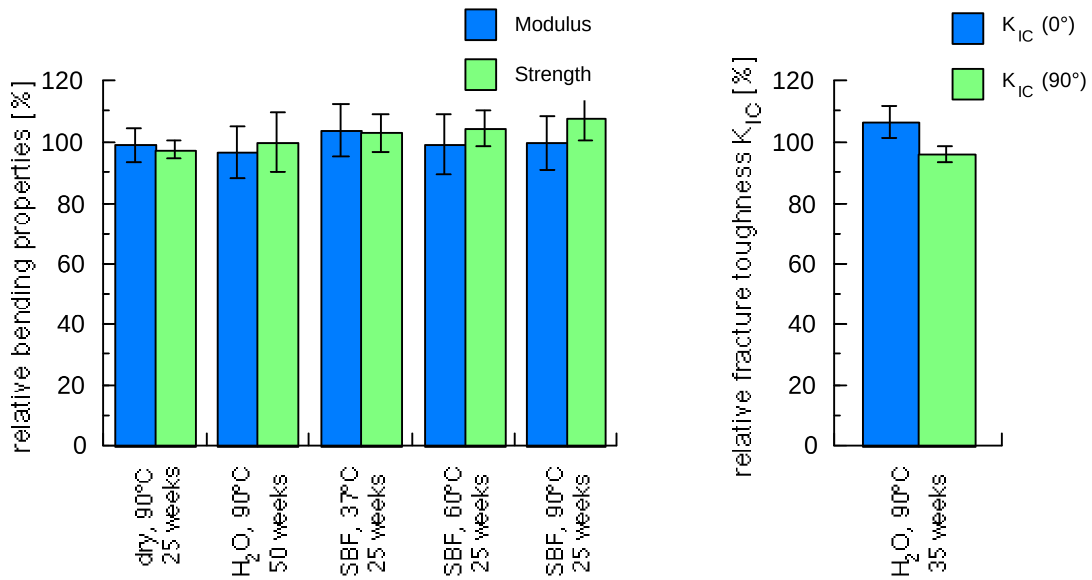

Fig. 2: Environmental Effects on the mechanical properties of knitted CF reinforced PEEK. Exposure in water or SBF at 37, 60 and 90°C for up to 247 days caused no significant changes. Reference values of unexposed material: bending strength = 530 MPa, bending modulus = 58 GPa, K_{IC} (0°, i.e. load in wale, crack in course) = 53 $MPa\cdot m^{1/2}$, K_{IC} (90°, i.e. load in course, crack in wale) = 24 $MPa\cdot m^{1/2}$.

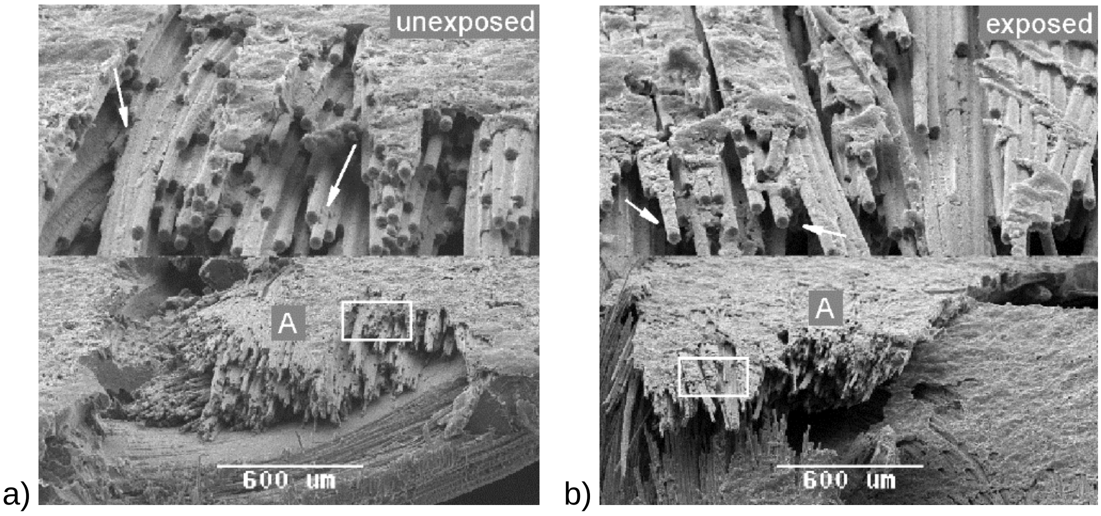

Fig. 3 *Fracture area (tension surface) of knitted CF reinforced PEEK 4-pt bending specimens before (a) and after (b) long-term exposure to H2O at 90°C for 50 weeks. Short fiber pull-out lengths were observed at the fracture surface of fiber bundles (A), thus indicating high fiber/matrix interface adhesion.*

Knitted GF reinforced PET:
After short exposure times, an important decrease of the macroscopic flexural properties was observed (Fig. 4). The same reduction as for the microscopical bending strength was found for fiber/matrix interfacial debonding shear strength (IDSS) determined by single fiber push-out.

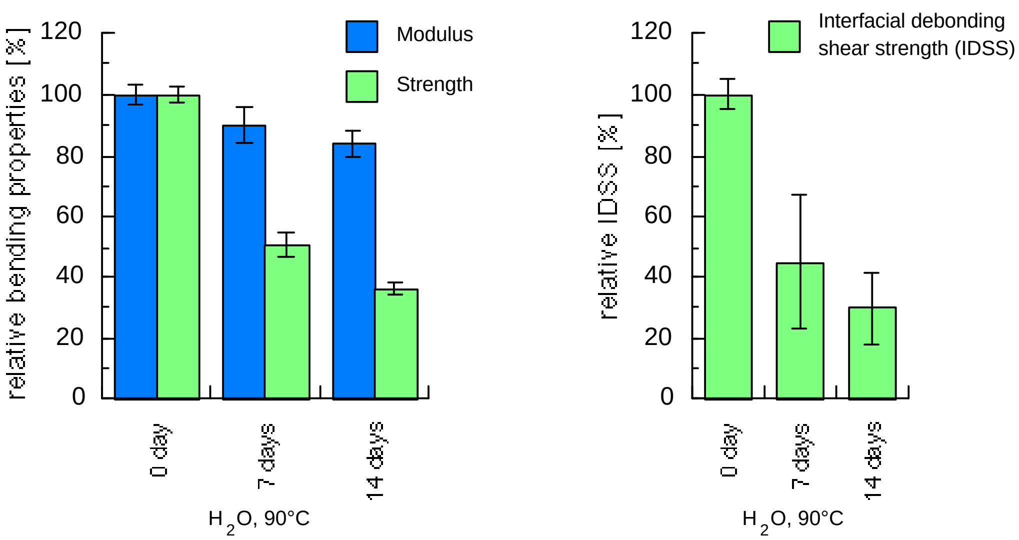

Fig. 4: *Significant drop in macromechanical (flexural) and micromechanical (interfacial debonding shear strength IDSS) were observed with GF/PET after very short exposure times to H_2O at 90°C. Reference values of unexposed material: bending strength = 328 MPa, bending modulus = 22 GPa, IDSS = 60 MPa.*

The macroscopical fracture surfaces (4-pt bending) of unexposed and exposed GF/PET knits are presented in Fig. 5. More brittle matrix failure and reduced fiber/matrix interface adhesion was observed as a consequence of hygrothermal degradation. This was confirmed by push-out experiments (Fig. 6).

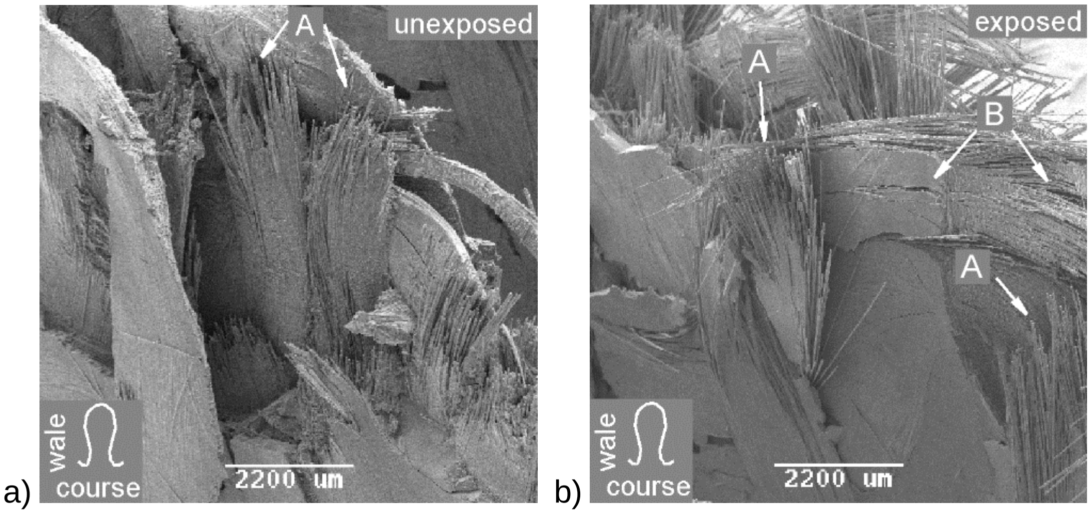

Fig. 5: Fracture surfaces of GF/PET knits before (a) and after (b) exposure in H2O at 90°C for 2 weeks. Significantly reduced interface adhesion is indicated by increased fiber pull-out lengths (A) and transverse splitting of loop heads (B) in exposed samples (b).

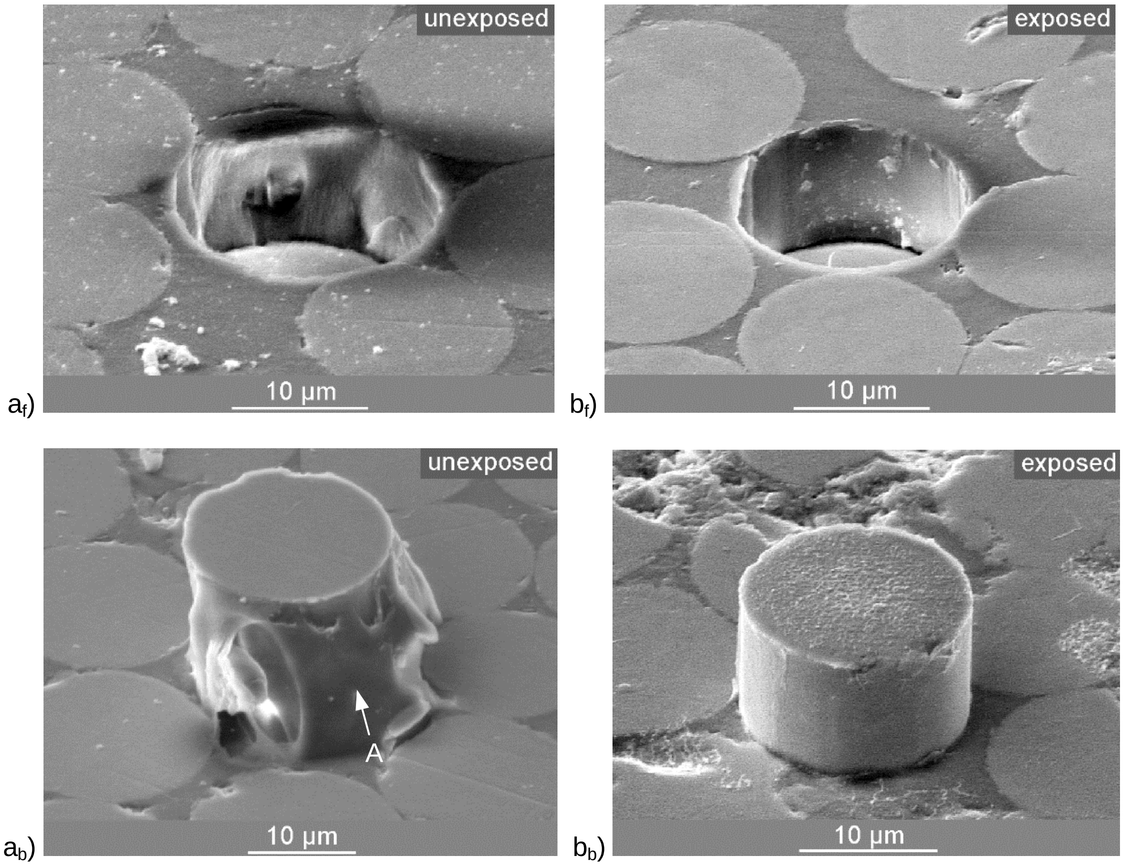

Fig. 6: Pushed-out fibers on the front (top) and backside (bottom) of thin (100 – 200 µm) push-out samples, taken from unaffected areas of tested 4-pt bending specimens. Ductile failure, involving a polymeric interphase (A) was observed in unexposed

GF/PET (a), while brittle failure at much lower interface debonding stresses (see also Fig. 4) occured after exposure (b).

DISCUSSION

Knitted CF reinforced PEEK: Long-term exposure to SBF and water at elevated temperatures caused no significant changes on failure behavior and mechanical properties. Beside of the excellent enviromental resistance of CF/PEEK, the structure of KFRCs may contribute to this result. Even though the properties of KFRCs are matrix directed [15], there is no distinctive transverse direction as in unidirectional composites. Therefore, small decreases in matrix and/or fiber/matrix interface properties may not become apparent in the macroscopic mechanical properties of KFRCs.

Knitted GF reinforced PET: Hygrothermal exposure of knitted GF reinforced PET lead to a significant reduction of its mechanical properties, determined by 4-pt bending and push-out experiments. The decrease was related to severe hydrolytic matrix and fiber/matrix interface degradation. The similar relative decrease of interface debonding strength and macroscopic bending strength (Fig. 4) can be understood with respect to the structure of KFRCs. Knitted fiber bundles can be modeled as straight and curved beams, as proposed by de Haan [15]. A weakness of either the matrix or the interface reduces the strength of the fiber bundles in the intermeshing area and consequently of the complete structure. Defects in the intermeshing area were indicated by de Haan as strength reducing factors of the macroscopic structure. Therefore, interface and matrix strength is correlated with the macroscopic strength of KFRCs.

CONCLUSIONS

Knitted CF reinforced PEEK exhibits excellent environmental stability in body fluids and water at elevated temperatures. In the presented work, no significant effect of longterm exposure on fracture toughness and flexural properties of CF/PEEK knits was found. It is concluded that the studied material, therefore, is highly appropriate for load-bearing implants and other high performance applications with comparable environmental conditions. In contrast to the outstanding environmental resistance of CF/PEEK, knitted GF reinforced PET was found to be considerably affected by hygrothermal exposure. With respect to automotive applications, the environmental sensitivity of GF/PET has to be addressed by avoiding moisture contact. Even though the hydrolysis of PET is slower at lower temperatures, the temperatures at which cars are regularly exposed to are relatively high (e.g. during insolation). Considering a 50% reduction of bending properties, determined after one week in water at 90°C, it has to be expected that over the life time of a car, moisture and service temperatures would cause degradation effects strong enough to reduce the performance of GF/PET to a critical level.

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