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DEVELOPMENT OF DESIGNABLE INTERFACE ADHESION POLYMER COMPOSITES

PHD THESIS BOOKLET

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1. INTRODUCTION

Composites were well-known to humanity before the dawn of time. It is recorded that in ancient Babylonia and Egypt, various composite products (adobe bricks) were already available, which followed the basic idea of combining and combining the properties of a material that are beneficial to us [1]. Of course, the mechanical properties and durability of these early composites are orders of magnitude lower than those of the high-performance composite products used today.

Polymer composites were first used by the military industry during the Second World War. During the war, there was an increased demand for new materials to be used in the manufacture of various military equipment. In the UK, the fuselage of the Spitfire aircraft was made from aluminium, but dwindling aluminium supplies led to the use of polymer composites reinforced with flax fibre in prototype production. After the military industry, polymer composite parts were introduced into the automotive industry for various sports cars in the years immediately after WWII, in many cases still using fibreglass reinforcement. Carbon fibre-reinforced polymer composites first appeared in motorsport in the 1981 season, thanks to a development by the McLaren Formula 1 team. The main concern was to achieve adequate safety with minimum weight. The development of safety is illustrated by the fact that the use of composites has led to a drastic reduction in fatal accidents in the sport after their introduction [2]. Nowadays, composite products, including high-performance carbon fibre-reinforced materials, can be found in most areas of life, including aircraft, passenger cars, sports equipment, medicine and construction [1, 3-5]. This is because the use of carbon fibre-reinforced composites can further reduce density, which has led to the replacement of structural steels by composite parts in some areas [6].

However, the use of carbon fibre-reinforced polymer composites is limited by the fact that they exhibit brittle behaviour with minimal toughness during failure. In general, a material is said to be more ductile if it exhibits significant deformation before failure is reached, thereby increasing the energy absorption capacity of the system. In engineering, we use the term toughness to refer to the resistance of a material to crack propagation and its energy absorption capacity. Materials with ductile properties are capable of more significant deformation and, thus, greater energy absorption than their brittle counterparts. While metals typically exhibit a gradual failure (brittle fracture may of course, occur depending on the stress), carbon fibre polymer composites exhibit an unprecedented, catastrophic brittle failure.

Why is toughness so important? Part a) of Figure 1 shows a picture taken during the free practice session of the 2018 British race of Formula 1, during which the front suspension of the racing car broke due to a sudden overload. You can see the destruction associated with the high energy release; the rocker arms exploded almost immediately due to the sudden high load. As a result, the pilot did not have the opportunity to react to the emerging error. This behaviour can also be observed in the picture b) of Figure 1, where the failure of a wind turbine blade can be seen. Here, however, a tougher fracture can be observed in part, thanks to the hybrid reinforcement used. In addition to the carbon fibre reinforcement, glass fibre reinforcement was used. Thanks to the tougher behaviour, the structural integrity can be maintained even at higher deformation levels, thereby increasing the system's reliability.

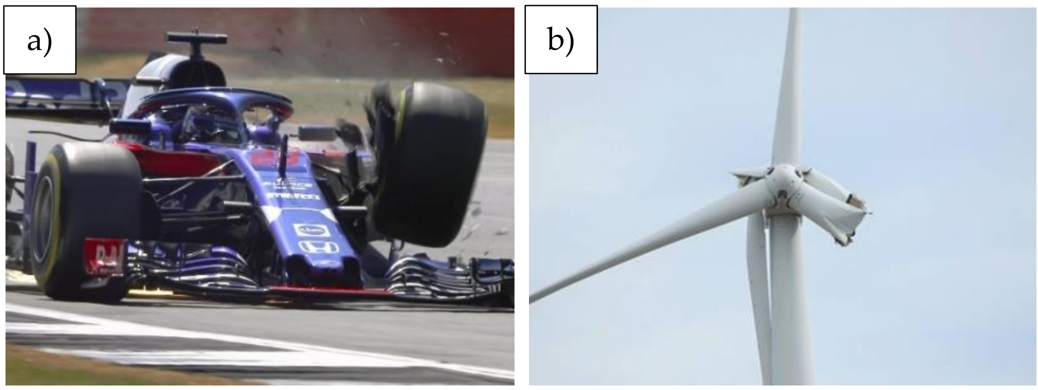

Figure 1. a) Breaking the suspension of a Formula 1 car due to overloading [7]; b) Wind turbine with broken blade [8]

My dissertation aims to research and examine a procedure that can be used to make the damage process of composites more favourable and tougher, by avoiding catastrophic failure while increasing the system's reliability. The aim of the research was to develop a novel toughening process. During the first step of the work, with the help of a general literature review, I explained the methods used so far in achieving the ductile behaviour at composites. Then, I selected the favourable research directions based on the results so far. During the research work, I examined the legitimacy of the method I used, during which I tried to verify my previously established hypotheses. Finally, I concluded my thesis with the theses I had drawn up during my research work.

2. CRITICAL ANALYSIS OF THE LITERATURE, OBJECTIVES

It is also clear from the literature review that researchers have been working on improving and inducing the ductile behaviour of composites for decades, starting with hybrid reinforcements. A significant breakthrough in the subject has yet to be achieved since then, although, in addition to hybrid reinforcement, several methods have been deeply researched over the years. In each case, the composite's mechanical properties must be sacrificed to achieve ductile behaviour. In most cases, this is its strength or modulus.

In most cases, research comprehensively examines the relationship between thermoplastic material and cross-linked material. In some cases, the resulting structure can even be structured with the help of 3D printing. The possibility of this and the resulting structure and its effect on the interface are therefore worth investigating in every way. In this case, the ductile behaviour can result from the tougher behaviour of the thermoplastic layer, and, as several studies have shown, its effect on the interfacial shear strength.

Several options for achieving ductile behaviour were given in the literature. The research can be classified in terms of the methods used, according to which phase of the composite was modified to achieve a more ductile behaviour. In the case of modifying the reinforcing structure, most of the literature achieved a tougher behaviour with the help of hybridization (association of fibres with a higher deformation capacity next to carbon fibres). Another option is to toughen the resin system with additives. The method can be further divided into two subgroups, using rubber or thermoplastic additives. With the help of additives, the crack propagation can be altered, and the deformation capacity of the matrix can also be increased. Another option is the introduction of inter-layers to achieve a more ductile behaviour. In the case of inter-layers, several solutions appeared, which were also diverse regarding the materials used. The geometry of the layers placed between the reinforcing layers also played an essential role during certain research, which was an important parameter not only in the case of interlayers (printed interlayer materials) but also in the case of processes based on the interruption of fibre continuity.

Furthermore, many researchers have dealt with matrixes with interpenetrating polymer networks, with the help of which the desired tougher behaviour was achieved. In this case, the true nature of the appearing IPN system was not examined; presumably, in many cases, only blends appeared, where the phases were able to cooperate reasonably; thus, the hybrid effect was able to appear minimally. However, the double continuous phase structure was only investigated in a few cases.

The possibility of repairing damaged composite parts has also become an exceptionally researched topic in recent years. There are several approaches to repair damaged or broken parts. Regarding their classification, we can talk about methods that do not require external action and techniques that require external action. In the latter's case, some activation energy is required to create the repair. In most cases, this is heat, which in some cases has been combined with pressure. A fundamental principle on the subject was the same for all research: the applied temperature, which must be above the T_m of the thermoplastic layer but below the T_g of the applied resin system. In addition, it is crucial to determine the required time and the effect of the pressure applied during the repair on the healing time. By modelling the healing process, an optimal time could be determined to fill in the gaps, so I also set the goal of describing this process.

In the case of carbon fibre/epoxy resin systems equipped with thermoplastic interlayer material, tougher behaviour and improved damage process can be achieved simultaneously. Therefore, during my research work, I investigated the effect of systems associated with thermoplastic material on the behaviour of the composite system, taking into account several aspects. However, with the addition of the thermoplastic material, not only the tough behaviour changes but also the emerging phase structure and the relationship that occurs at the interface, the knowledge of which provided an important basis for my research and fills a gap in the literature.

Based on the above, I defined the following goals for my research:

- Designable change of interfacial shear strength by changing the boundary layer along the length of the fibres using a thermoplastic additive, which can be used to alter properties between fibre-matrix and layer-layer.
- Investigation of the effect of different interlayer material concentrations on fracture toughness.
- Examination of composites created with thermoplastic layers of different patterns.
- A deeper examination of the parameters of healing/repair, during which I would examine the change in healing efficiency depending on the applied pressure and concentration.

My research work hypothesized that the hybridization effect that also occurs with IPNs could be designed between PCL and epoxy resin structured with the help of 3D printing, which can be used to improve the ductile behaviour of composites. Furthermore, with the help of a thermoplastic material, in addition to toughening, damaged composites can be repaired, where the repair parameters can be optimized.

Figure 2 summarizes the theses formulated during the research work and the path leading to them.

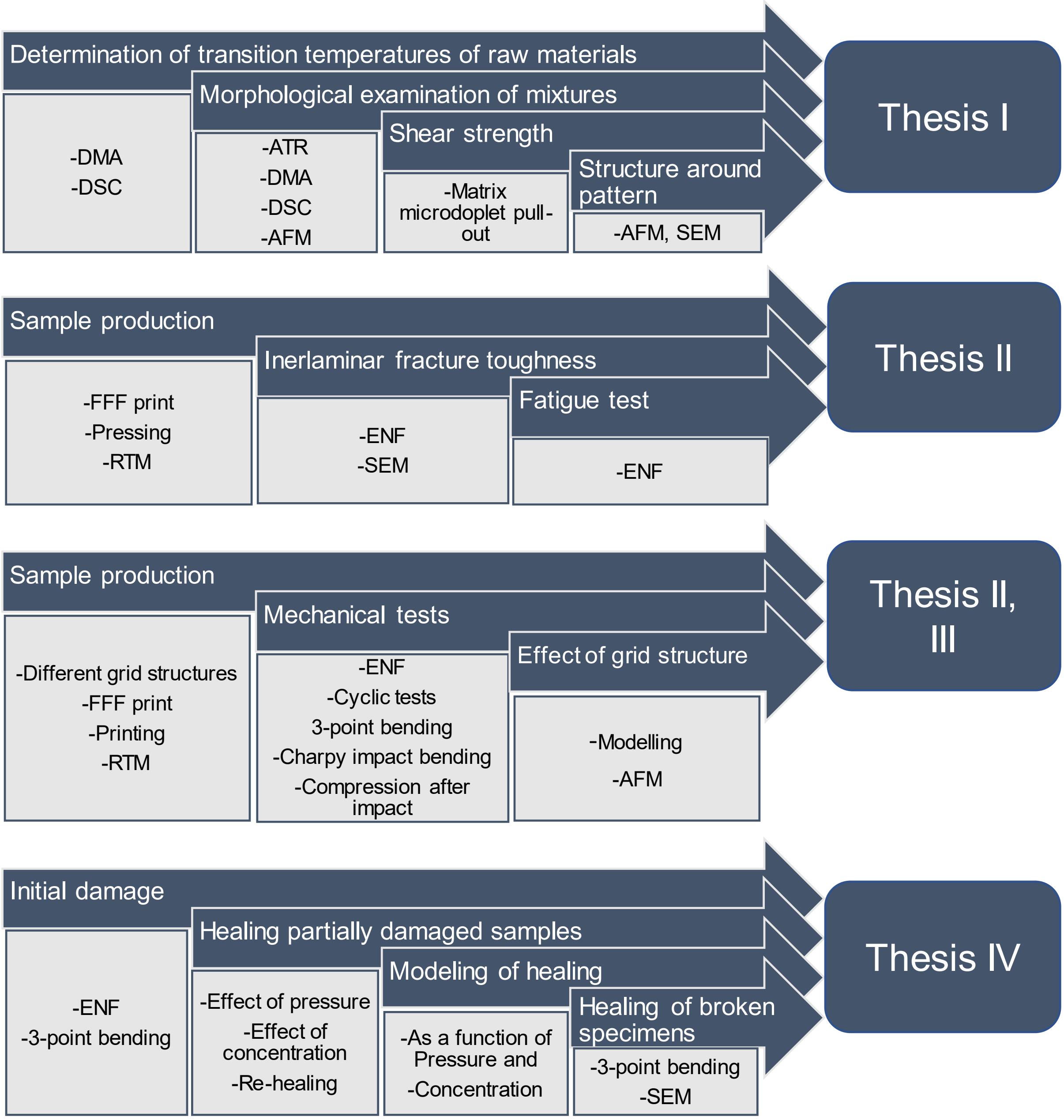

Figure 2 The relationship between the research work carried out during the dissertation and the formulated theses

3. MATERIALS AND METHODS

This chapter presents the raw materials for the composites used in my experiments. I also describe the testing equipments used, their operation, and the settings used in my work.

3.1. Materials

Fibre reinforcement

- PX35 FBUD300 (Zoltek Zrt., Nyergesújfalu, Hungary) unidirectional (UD) carbon fibre reinforcement (areal density: 309 g/m^2), with Panex35 50k rovings, average fibre diameter 8 μm
- Sigratex KDK 8042 (SGL Technologies GmbH., Meitingen, Germany) biaxial carbon fabric (areal density: 200 g/m^2), sized to epoxy resin, with 3k rovings, average fibre diameter 8μm.

Resins

- IPOX ER 1010 (IPOX Chemicals, Budapest, Hungary) Bisphenol-A-diglycidyl ether (DGEBA) resin (viscosity at 25 °C: 10000–14000 mPa·s) and IPOX MH 3111 (IPOX Chemicals, Budapest, Hungary) as hardener, viscosity at 25 °C: 80–120 mPa·s. Mixing ratio was 100:75 by weight. Resin hardening was carried out at 90 °C for 3 hours.
- IPOX MR 3012 (IPOX Chemicals, Budapest, Hungary) aliphatic epoxy resin (viscosity at 25 °C: 100-200 mPa-s) and IPOX MH 3124 amine-based crosslinking component (viscosity at 25 °C: 80-120 mPa-s). The mixing ratio was 100:40 by weight, according to the manufacturer's recommendation.

Interlaminar material

eMorph175N05 emorph filament (Esun Industrial Co., Ltd., Shenzhen, China), 0,5 kg/roll; diameter of filament: 1,75 mm. Printing temperature 180 °C (T_m≈65 °C).

3.2. Methods

Three-point bending test

I performed the measurements according to the MSZ EN ISO 14125 standard. During loading perpendicular to the fibre direction, I examined the behaviour of the composites at a support distance of 80 mm and a test speed of 5 mm/min. During the tests, I used standard 120x15 mm test specimens.

The tests were performed on a Zwick Z005 universal material testing device on a three-point bending support.

Charpy impact test

I measured according to the MSZ EN ISO 179-2 standard. With the help of the instrumented impact test, I tested the resistance of the composites against a sudden shock-like impact on test specimens supported at a distance of 62 mm, with an energy of 15 J and an impact speed of 3.7 m/s, in the face of an impact. During the impact strength test, the energy absorption capacity of the material can be tested, i.e. the toughness of the given material. This can be determined by the energy consumed during the impact. For the Charpy test, I used 80x10 mm specimens.

End-notched flexure

Based on the ASTM D7905 standard, I performed the tests in a 3-point bending arrangement. With the help of the measurement, I examined the effect of the thermoplastic material on the interlayer properties. Teflon film (PTFE-Poly(tetrafluoroethylene) with a thickness of 2 μm (Airtech International Ltd., California, USA)) was used to create the initial defect. The test speed was 5 mm/min; the support distance was 120 mm. The average width of the specimens was 25.4 mm, and their length was 163 mm. Markings were painted on the side of the test specimens at 1 mm intervals to facilitate the evaluation. I recorded the measurements with a Nikon 600D digital camera to accurately monitor the damage. The camera took 60 photos per second.

Fatigue test

I performed the fatigue measurements on specimens corresponding to the ENF test in a three-point arrangement. The study aims to examine the long-term resistance of the composites. The test frequency was 5 Hz.

Differential scanning calorimetry

I performed DSC tests on the epoxy resin-PCL mixtures with different weight ratios using Q2000 equipment. The weight of the tested samples varied between 3-6 mg. I evaluated the evaluation with TA Universal Analysis 2000 software. The temperature range of the measurements was -80-100 °C, with nitrogen purging at a flow rate of 50 ml/min, using a heat/cool/heat cycle at a speed of 20 °C/min.

Dynamic mechanical analysis

During the material structure tests, 5 Hz, 2 °C/min, with a three-point bending arrangement, I performed tests in the temperature range between -75 °C and 125 °C. The dimensions of the test specimens were 56x13x3 mm. To produce the test specimens, I made a silicone tool to pour the various PCL-epoxy resin mixtures.

Compression after impact

- To create the initial damage, I used a CEAST FRACTOVIS 9350falling weight impact tester, a drop height of 1 meter and a total weight of 25 kg with a M3144 22 kN type dart.
- The compression tests were performed with a Zwick Z050 universal material testing device using a compression after impact (CAI) instrument. The width and height of the specimens used during the measurements were 80 mm. The test speed was 2 mm/min during the measurements; due to the tool's design, the maximum distance the loading machine could move in the "z" direction was 10 mm. During the examination, I used a two-camera 3D Digital Image Correlation (DIC) system to accurately determine the spatial deformation (Mercury Monet).

Matrix droplet pull out test

The tests were performed with a Zwick Z005 universal material testing device with a 20 N load cell. I performed measurements with a device developed for drop removal during the tests. The test speed was 2 mm/min, and the distance between the scraper blades was 30 μm.

Statistical methods

- ANOVA – analysis of variance
- Paired T test

4. STRUCTURE OF THE REASEARCH WORK

During the first part of the research, I scrutinized the micromechanical behaviour of composites, during which I examined the relationship between the thermoplastic PCL and the epoxy resin and its effect on the value of the interfacial shear strength at the fibre-matrix interface. In the next step, I examined the emerging phases, where I created a PCL-rich structure with the help of 3D printing, which I poured around with epoxy resin. Figure 3 schematically shows the work done in the first part of the research (work done for thesis I).

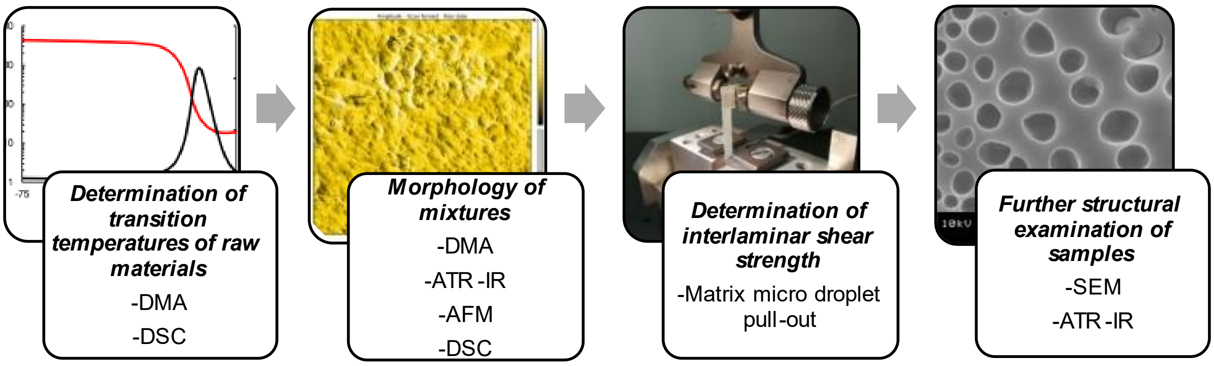

Figure 3 Schematic overview of a series of experiments related to the effects of the interlayer material on the properties of composites at the micro level

In most cases, the improvement of the interlayer toughness properties of composites can be achieved with the help of intermediate layers placed between the reinforcing layers. With the help of intermediate layers (inter-layers), the shear strength between the reinforcing layers can be improved. Thanks to this, the probability of catastrophic failures can be reduced. In most cases, thermoplastic material was used for this in the literature. This is also possible with PCL, which I printed in different designs on carbon fabrics, examining the effect of the surface concentration of PCL in terms of the energy required for crack propagation (Figure 4) (work for thesis II).

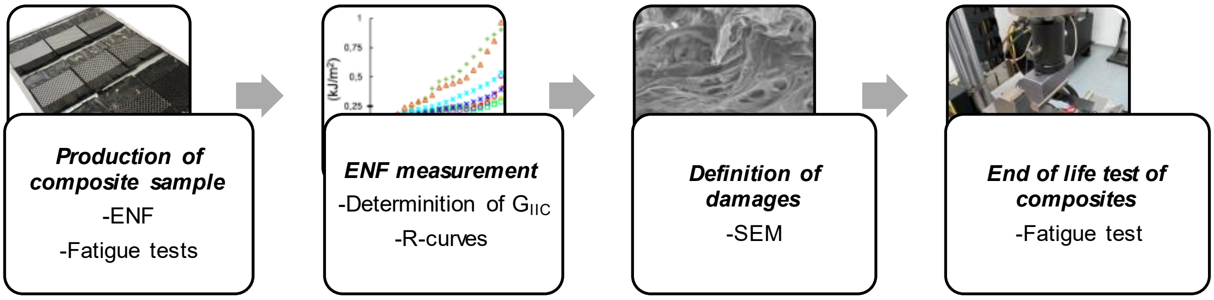

Figure 4 Schematic overview of a series of experiments regarding the effects of interlayer material on interlayer properties

In the ENF and fatigue tests, the interlayer adhesion modifying material changed the interlaminar fracture toughness behaviour. The reason for this is the slowing down of crack propagation and the gradual progression of its course. Thanks to this, the final failure occurred at a higher deformation level, during which the system could absorb additional energy, increasing the degree of ductile behaviour. For a deeper interpretation, I carried out quasi-static and dynamic measurements, with the help of which I investigated the further effect of the surface filling on the mechanical behaviour of the composites (Figure 5) (work for thesis II-III).

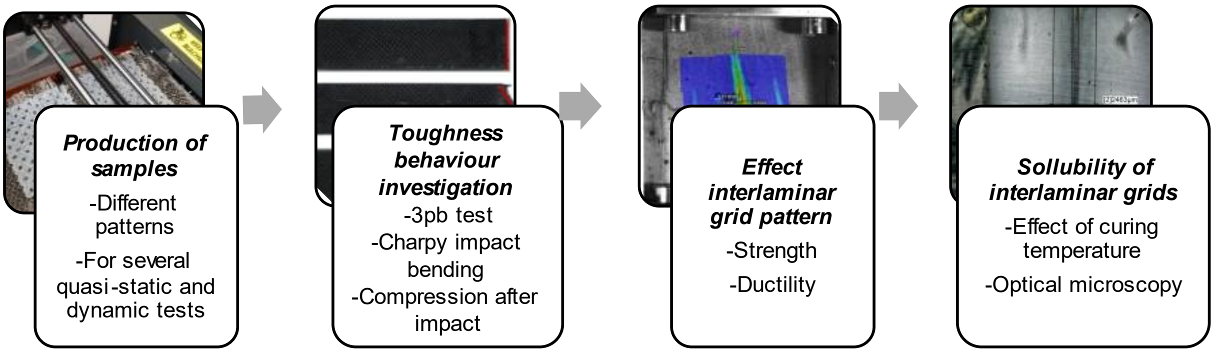

Figure 5 Schematic overview of a series of experiments, during which I investigated the effect of the pattern of the interlayer material on the mechanical properties of composites

The intelligent behaviour of composites has already been dealt with in numerous technical articles, especially in recent years. In most cases, the focus was on the strength properties that develop after healing. However, the literature regarding optimising healing, repair, or modelling still needs to be completed. In most cases, the healing of composites with a thermoplastic layer or partial-IPN matrix is not precisely defined. In most cases, this setting is only linked to the temperature T_m of the thermoplastic layer, i.e. it is sufficient to cure the composites only above the melting temperature of the interlayer material. However, the duration or pressure dependence of this has not been revealed. I used ENF tests at different pressures (based on appropriate technologies) and at different surface concentrations (thesis IV) to model this (Figure 6).

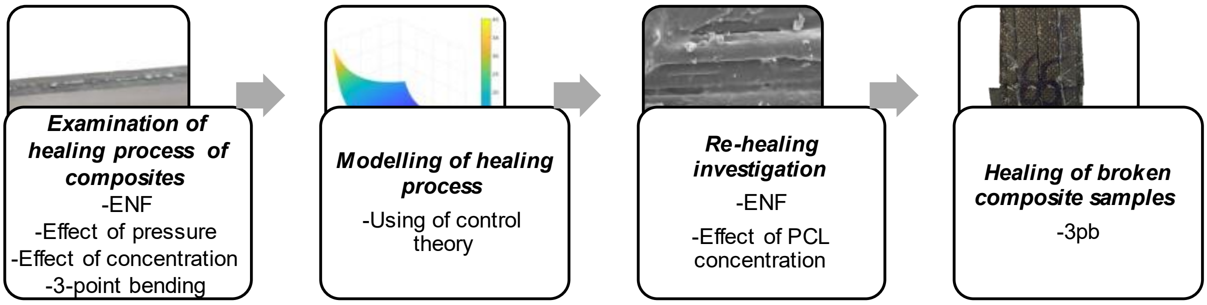

Figure 6 Schematic representation of a series of experiments during which I investigated the healing of the composite system

5. Summary

Nowadays, the dominance of carbon fibre-reinforced polymer composites is unquestionable. Their spread is hindered by their high cost and sudden, explosive, catastrophic failure due to overload and brittle behaviour. There are many ways to improve the latter; in my dissertation, I examined the effect of 3D-printed thermoplastic interlayers on the mechanical properties of composites. Furthermore, I discussed the relationship between the applied resin and thermoplastic material and its impact on the interfacial shear strength. Again, with the help of the printed samples, I observed the change in the mechanical and ductile behaviour of the composites modified with an interlayer, which I supplemented by modelling the repair of the composite systems.

Based on the processed literature, it can be seen that there are many approaches to achieving ductile behaviour. The most common method is using fibres with higher energy absorption capacity associated with carbon fibres, i.e. hybridization. I classified the procedures according to which composite component the researchers achieved a tougher behaviour by modifying. Thus, I categorized the methods into three classes: modification of the reinforcing structure, matrix toughening, and introduction of interlayers. A common point in all methods is that other beneficial properties of composite systems had to be sacrificed to achieve a tougher behaviour; in most cases, their load capacity was weakened when reaching a tougher behaviour.

In the second half of the literature review, I examined the healing ability of cross-linked matrix composites (Chapter 2.3). The repair/healing of composite systems can be divided into two classes: methods that require external action and methods that do not require external action. In the case of the latter, three known methods have appeared: microencapsulation, hollow fibre and vascular methods. In the case of methods that do not require external action, it is expected that the system reacts to the cracks and inhomogeneities that develop and, in most cases, fills the discontinuity with the same resin as the cross-linked system, and then healing occurs with its cross-linking. In cases requiring intervention, the healing substance must be activated, and energy must be invested. In most cases, heat was used for this, during which, just like in the previous point, the formed cracks were filled with the healing substance. They have in common that the healing material is usually a thermoplastic material, which can even be used to toughen composites.

In a significant part of the publications dealing with the change of ductile behaviour, a method (inter-layers) was used to achieve a more favourable failure. I saw significant research potential in the subject area. The publications appearing in the second half of the literature review on healing methods requiring external intervention had in common that the researchers have not examined the healing process in depth. The process raises many unanswered questions, which I set out to investigate.

During the first step of my research work, I examined the feasibility of designable partial-IPN systems. To do this, I first examined the phases formed on different epoxy resin and thermoplastic material mixtures. During the tests, I created IPN zones within the resin in a structured way with the help of 3D printing, with the help of which I locally changed the resulting interfacial shear strength between the resin and reinforcing fibres, as well as modified the inter-layer connections using the printed intermediate layers. Thanks to this, I simultaneously realized the toughening of the matrix with a thermoplastic material, applied the interlayer technology with the help of 3D printing, and also reduced the probability of fibre breaks by changing the interfacial shear strength.

I examined the mode II interlaminar properties in the second part of the research work with the help of measurements up to failure. By increasing the material concentration of the thermoplastic, IInd mode fracture toughness value increased significantly, and a gradual type of failure appeared with stable crack propagation. This also occurred during the fatigue tests, where increasing the thermoplastic material concentration significantly increased the lifetime of the composites.

In the third stage of the research work, I investigated the effect of the pattern of the interlayer material created with the help of 3D printing on the strength and ductility of the systems. I found a critical zone distance in terms of the patterns, below which the strength values decrease significantly, approximating the properties of PCL matrix composites. This appeared because the IPN zones between the pattern lines began to touch during crosslinking, resulting in a phase inversion between the patterns. In the chapter, I also examined the crosslinking temperature for the critical zone distance. By increasing the crosslinking temperature, I found that the PCL samples fuse faster, i.e., the vital zone distance appears at a greater distance.

In the fourth stage of the research work, I examined the healing process of composites on partially damaged and fractured composites. In the case of the former, I discussed the process with different interlayer material concentrations and pressures applied during other healing methods. By increasing the pressure and the concentration of thermoplastic material, the healing process is accelerated, and the resulting inhomogeneities are filled sooner. I modelled the process by connecting a single-storage proportional member and a dead-time member in a series. In the third stage of the research work, I examined the concentration-dependent curability of the fractured samples. By increasing the concentration of PCL, a limit value appeared in terms of flexural strength, which approximated the properties of the composite containing only PCL matrix material. This happens because the thermoplastic material cannot heal the broken fibres and the damage created in the epoxy resin. By filling in the inhomogeneities, the properties of the thermoplastic material composites appeared. Of course, during the second loading cycle, these points were dangerous places, so the material properties appearing there dominated.

5.1. Theses

Thesis I:

I have demonstrated that a gradient phase structure is formed between the DGEBA-type epoxy resin matrix and PCL used for local surface treatment of reinforcement fabric by 3D printing during crosslinking, which locally modifies the interfacial shear strength. The structured modification of the surface treatment provides an opportunity for a structurable design of the interfacial shear strength between the matrix and the reinforcing material.

My claim was verified on composites built up from Zoltek PX35 FBUD0300 type UD carbon fibres, Ipox ER 1010; MH 3111 epoxy resin matrix and eMorph175N05 polycaprolactone material.

Publications related to this thesis:

- ***B. Magyar,*** *T. Temesi, G. Szebényi: Szénszál erősítésű kompozitok szívósságnövelése a határfelületi adhézió módosításával 'XXV. Nemzetközi Gépészeti Konferencia (OGÉT 2017). Kolozsvár, Románia', 25, 263-266 (2017)*
- *Szebényi G., Czigány T.,* ***Magyar B.****, Karger-Kocsis J.: 3D printing-assisted interphase engineering of polymer composites: Concept and feasibility. Express Polymer Letters, 11, 525-530 (2017) 10.3144/expresspolymlett.2017.50 IF:3,064 Q1*
- *G. Szebényi,* ***B. Magyar****, T. Czigány: Comparison of different interfacial engineering methods to achieve pseudo-ductile behaviour of carbon fibre reinforced polymer composites 22nd International Conference on Composite Materials 2019 (ICCM 22). Melbourne, Ausztrália (2019), Mouritz, A - Proceeding of International Conference on Composite Materials (ICCM22) (2019) pp. 1-9. Paper: 1209-1, 9p., 1209-1*
- *Szebényi G.,* ***Magyar B.,*** *Czigány T.: Achieving Pseudo-Ductile Behavior of Carbon Fiber Reinforced Polymer Composites via Interfacial Engineering. Advanced Engineering Materials, 23, 2000822/1-2000822/7 (2021) 10.1002/adem.202000822* ***IF:3,217 Q2***
- ***Magyar B.****, Szebényi G., Hliva V.: Decomposition and thermal properties of inter-layer modified polymer composites, Flame Meeting on Fire Retardant Polymeric Materials, FRPM21, Budapest, 2021. august 29-september 1.*

Thesis II:

On carbon fibre reinforced unidirectional composites, I demonstrate that a locally placed interlayer reduces the interfacial shear strength between the fibre-matrix, thereby creating zones of higher energy absorption due to fibre-matrix separations, which reduce the probability of fibre rupture, thus resulting in catastrophic failure occurrence at higher deformation levels. On the other hand, the locally placed pattern further slows down the propagation of the crack due to its plastic deformation.

Due to the behaviour displayed,

a) with an increase in the concentration of thermoplastic material, the critical interlayer fracture toughness increases in direct proportion,

b) the apparent ductility increases proportionally with increasing thermoplastic material concentration, showing saturation at a zone spacing of 1.8 mm, reaching the values of the thermoplastic matrix reference specimens. This is due to the fusion of the locally located interlayer zones during cross-linking.

I verified my claim on composites built up from Zoltek PX35 FBUD0300 type UD carbon fibres, Ipox ER 1010; MH 3111 epoxy resin matrix and eMorph175N05 type polycaprolactone interlayer material, where the printed pattern height was 0.2 mm during printing. The crosslinking time was 3 h in a 90 °C oven.

Publications related to the thesis:

- *Szebényi G.,* ***Magyar B.,*** *Iványicki T.: Comparison of static and fatigue interlaminar testing methods for continuous fiber reinforced polymer composites. Polymer Testing, 63, 307-313 (2017) 10.1016/j.polymertesting.2017.08.033* ***IF:2,247 Q2***
- ***Magyar B.,*** *Szebényi G., Czigány T.: Metal-alike polymer composites: the effect of inter-layer content on the pseudo-ductile behaviour of carbon fibre/epoxy resin materials. Composite Science and Technology. 2021;215:109002 (2021), 10.1016/j.compscitech.2021.109002* ***IF:7,094 D1***
- *Szebényi G., Hliva V.,* ***Magyar B.****: Development of interphase engineering techniques for the ductility improvement in CF/EP composites - Comparison of NDT methods for delamination localization. Materials Today: Proceedings, 34, 113-116 (2020) 10.1016/j.matpr.2020.01.403*
- ***Magyar B****., Szebényi G.: Szénszál erősítésű kompozitok szívósságnövelése módosított határfelületi adhézió segítségével, Erősített műanyagok 2018 Nemzetközi BALATON Konferencia, Hungary, Balatonkenese, 2018. may 15-27.*

Thesis III:

I have demonstrated that the maximum strength of polycaprolactone-modified intermediate-layer carbon fiber-reinforced epoxy resin (DGEBA) composites modified by 3D printing depends on the printed interzone spacing and can be described by equations 1) and 2),

$$\sigma_{norm} = \frac{z^{b_n}}{{K_{0,5}}_{(T)}{}^{b_n} + z^{b_n}} \tag{1}$$

$$\sigma_{(z)} = \sigma_{norm}(\sigma_{max} - \sigma_{min}) + \sigma_{min} \tag{2}$$

σ_{norm} *is the normalized strength (-), z is the zone distance (mm),* b_n *is the system constant (-) (determined by the least squares method),* $K_{0,5}$ *is the critical zone distance (mm) (determined by the least squares method),* $\sigma_{(z)}$ *is the zone distance dependent maximum strength (MPa),* σ_{max} *is the ultimate strength (MPa) of the EP/CF composite. At the same time,* σ_{min} *is the ultimate strength (MPa) of the PCL/CF composite. The value of* $K_{0,5}$ *gives the critical initial zone distance at which a significant decrease in the normalized strength appears due to the meeting of the gradient phases formed around the printed zones during curing. The critical zone spacing that occurs depends on the curing temperature; by increasing it, the thermoplastic material mixes better with the epoxy resin so that the phases formed around the printed patterns can come together even between more considerable initial distances during curing.*

I have verified my claim on composites made of Zoltek PX35 FBUD0300 UD carbon fibres, Ipox ER 1010; MH 3111 epoxy resin matrix and eMorph175N05 polycaprolactone interlayer material, on samples with different PCL wt%, where the printed pattern height was 0.2 mm during printing. The crosslinking time of the samples was 3 h in oven at 85, 90, 95, 100 °C.

Publications related to the thesis:

- *G. Szebényi, **B. Magyar**, T. Czigány: Comparison of different interfacial engineering methods to achieve pseudo-ductile behaviour of carbon fibre reinforced polymer composites 22nd International Conference on Composite Materials 2019 (ICCM 22). Melbourne, Ausztrália (2019), Mouritz, A - Proceeding of International Conference on Composite Materials (ICCM22) (2019) pp. 1-9. Paper: 1209-1, 9p., 1209-1*
- *Szebényi G., **Magyar B.,** Czigány T.: Achieving Pseudo-Ductile Behavior of Carbon Fiber Reinforced Polymer Composites via Interfacial Engineering. Advanced Engineering Materials, 23, 2000822/1-2000822/7 (2021) 10.1002/adem.202000822 **IF:3,217 Q2***
- ***Magyar B.,** G. Szebényi: Polimer kompozitok károsodásának meghatározása újszerű módszerrel. Anyagvizsgálók lapja, III., pp. 71-74 (2021) ISSN: 1215-8410*
- ***Magyar B.,** Szebényi G., Czigány T.: Metal-alike polymer composites: the effect of inter-layer content on the pseudo-ductile behaviour of carbon fibre/epoxy resin materials. Composite Science and Technology. 2021;215:109002 (2021), 10.1016/j.compscitech.2021.109002 **IF:7,094 D1***
- *Szebényi G., Hliva V., **Magyar B.:** Non-destructive evaluation of interfacially engineered composites In: 20th European Conference on Composite Materials (ECCM20). Lausanne, Svájc (2022), Proceedings of the 20th European Conference on Composite Materials (ECCM20) - Composites Meet Sustainability (Vol 1-6) p. 62011*

Thesis IV:

I have developed a new qualification method suitable for characterizing the curing process of samples damaged in interlayer fracture toughness tests of carbon fibre-reinforced epoxy resin composites with polycaprolactone interlayer. The measurement procedure is based on observing the change in the critical interlayer fracture toughness. By observing the change in fracture toughness, the change in the healing process and its efficiency can be monitored.

It is shown that the healing process of damaged specimens of polycaprolactone interlayered carbon fibre reinforced epoxy resin composites in interlayer fracture toughness tests can be described by a composite element coupled in parallel with a proportional member, which is composed of a series-coupled dead-time and a single-container proportional member. The characteristic response function is given by (3):

$$X_{out_{(t)}} = A_{1_{(t)}} + A_{2_{(t-T_D)}} \left(1 - e^{-\frac{t-T_D}{\tau}}\right) \tag{3}$$

where, $X_{out(t)}$ is the response, i.e. the recovery efficiency (%); The proportionality factor A_1, whose value is constant during the process, is the G_{IIc} value of the damaged, untreated samples proportional to the original G_{IIc} value (%); A_2 proportionality factor, which gives the value of the maximum achievable healing efficiency (%); T_D dead time, the duration of the delay of the transient part (s); τ is the time constant (s). With the help of the equation, the time required for the effect to occur can be determined. However, it is not suitable for modelling the decrease in healing efficiency that appears when the thermoplastic material melts.

I verified my claim on composites made of Zoltek PX35 FBUD0300 UD carbon fibres, Ipox ER 1010 - MH 3111 epoxy resin matrix and eMorph175N05 polycaprolactone interlayer material, where the printed pattern height was 0.2 mm during printing. During the formation of the initial damage, I performed ENF tests up to a 2.5% power drop; I carried out the treatment at 65 °C.

Publications related to the thesis:

- *Szebényi G., Czigány T., **Magyar B.**, Karger-Kocsis J.: 3D printing-assisted interphase engineering of polymer composites: Concept and feasibility. Express Polymer Letters, 11, 525-530 (2017) 10.3144/expresspolymlett.2017.50* ***IF:3,064 Q1***
- ***Magyar B.**, Szebényi G.: Developement of pseudo-ductile composites via hybrid methods, Polymer Composites International Conference, Czech Republic, Tabor, 2019. may 14-16.*
- ***Magyar B.,** Szebényi G., Czigány T.: Metal-alike polymer composites: the effect of inter-layer content on the pseudo-ductile behaviour of carbon fibre/epoxy resin materials. Composite Science and Technology. 2021;215:109002 (2021), 10.1016/j.compscitech.2021.109002* ***IF:7,094 D1***

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7. MY PUBLICATIONS

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