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Developing nanostructured polymer matrix composites

Thesis booklet

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1. Introduction

In the 20th century, the evolution of technology required an increase in the performance of artificial engineering materials. The design and capacity of engineers is limited by the properties of the materials used. The toolkit of mechanical designers is greatly widened by the ever-growing composite materials, which can be used to increase the efficiency of certain structures and devices. From this point of view, polymeric composite materials are of the utmost importance, which are complex systems in which one phase is the reinforcement responsible for absorbing mechanical loads and the other phase is the embedding material, also known as the matrix. The latter's main task is to achieve a proper load distribution and to protect the reinforcing material (e.g. fibres or particles) from external influences. These materials are characterized by a relatively low density, in addition to their excellent mechanical properties, so that the weight of a particular device can be reduced by using them. This reduction in mass can lead to significant energy savings in almost all sectors of transport.

Carbon, glass or basalt fibre reinforced thermoset polymer composites often used in the automotive and aerospace industries, as well as in sports equipment, have a remarkably high mechanical performance and low density, but they exhibit a high level of rigidity compared to thermoplastic polymers and a number of ductile metals. In addition to developing superior strength properties in the field of high performance polymer composites, toughness enhancement and greater energy absorption are one of the major tasks of researchers.

The toughness of high-performance polymer composites is determined to a great extent by the properties of the embedding material so that the development of a matrix is reasonable with a higher mechanical energy absorbing ability than previously in addition to keep the good strength properties compared to the similar materials. To achieve this purpose, it may be particularly suitable to modify the matrix's micro and nano structure, which results in a reduction in the rate of generation and propagation of the cracks, thus increasing the resistance to cracking, i.e. toughness.

The creation of a micro- and nano-sized structure can be achieved by several methods, one of them is the formation of a mixture of immiscible polymeric materials, i.e. hybrid matrix materials. In this case, the aim is to influence the mixing of the material in such a way as to allow the creation of a novel material combination of a special structure, which is synergistic to the ingredients, which may have a phase structure in nanometre size range.

This can be achieved by associating different thermoplastic polymers or different types of polymeric resins. Preferably, the polymer mixture has a phase structure in which the two phases are connected to an extremely large surface (usually by second-order bonds). All of these can provide increased toughness and capability of resistance in case of impulse-like and dynamic loads not only to the blend but also for the composite material formed therefrom.

During my research, I aimed to develop and analyse the behaviour of duromer matrices with a nanoscale structure formed of immiscible polymeric resins. Using the advantageous features offered by the nanoscale structure, I aim to analyse and enhance the capability of resistance of these composites to impact and cyclical loads, thus creating more efficient and safer composites.

2. Short overview of the related literature, aims of the thesis

During the literature review, it was striking that many more literature publications related to the testing, qualification and modeling of blends and composites formed by thermoplastic polymers and their composites. This is especially true of duromers and their composites. The morphological qualification of the nanostructured so-called interpenetrating polymer network was included in many publications, but the mechanical and morphological examination and qualification of filled systems or composites formed from this type of blend is a scarce area. The potential inherent in this area can have a beneficial effect on the toughness of the composites and their responsiveness to cyclical stress due to the synergistic effects of the structure of the different hybrid resins.

During my research, I used the models associated with thermodynamic, morphological and failure analysis methods, which can be used to create and investigate high toughness and high strength composites. For the production of the hybrid systems, I would like to use the most respected synthetic resins in the industry: epoxy (EP), vinyl ester (VE) and unsaturated polyester (UP) resins. The EP resin has good mechanical properties, VE resin has relatively good chemical resistance, and UP resin is widely used and not least favourable in price. All three resins, together with their potential, have been published in connection with all three binary systems, which have analysed the phase structure that has been developed but their use as a composite matrix material has been devoted to little research. This is especially true for carbon fibre and hybrid reinforcement systems. From this point of view, it may be obvious to use the matrix material offered by hybrid resins in endless fibrous structures. In

my research, I plan to study this with carbon fibers and hybrid fibre reinforced systems besides various resin combinations.

During my work, I investigate the effects of the structures with the phase separation on the morphological structure of the highly cross-linked polymeric resins and their fibrous reinforced composites and its impact on the mechanical properties. From the results obtained, I would like to draw conclusions that could later serve to describe the properties of materials of similar structure.

As stated above, my goals can be taken to the following points:

1. In the case of two component hybrid polymer resin systems, determine the relationship between the phase structure and the mechanical properties (mainly toughness and strength).
2. Investigating the achievement of a remarkable non-strength-promoting toughness gain through the use of hybrid resin matrix in long fibre reinforced composites using the potential of the hybrid matrix material phase structure.
3. Investigate and analyse the responsiveness of hybrid resin matrix long-fiber composites to cyclical wear-bearing stresses, inferring all of these to the suggested areas of application.

3. Applied materials and experimental methods

Applied materials

In the selection of the types of material used to make the resin mixtures, it has been very important to have been successfully used in the production of nanostructured systems in the literature. The epoxy component used was ER 1010 (IpoX Chemicals), a bisphenol-A-diglycidyl-ether-based resin. The reason for this choice is that DGEBA is one of the most widely used epoxy groups currently in use. For the DGEBA resin, an amine type crosslinker was used with EH 2293 (IpoX Chemicals) with cycloaliphatic isophorone diamine construction. The epoxy resin was mixed with the amine type crosslinker in the stoichiometric ratio of the reagent groups

A further component of the mixed resins was AME 6000 T35 (Ashland Composite Polymers) bisphenol-A-methacrylate-based vinyl ester (VE) resin containing 35% styrene. When selecting the type of VE component, it was the decisive factor that nanostructured phase structures were successfully produced in the prior art with similar materials.

Another component of the blends was the unsaturated polyester resin based on DISTITRON 5119 ESX20ZQ (Polynt S.p.A.) orthophthaleic acid based with 40% of styrene. This choice is justified by the fact that it is one of the simplest chemically constructed and nowadays used in the highest amount of UP resin, which has a favourable price.

For the crosslinking of polyester and vinyl ester resins, the diisobutyl phthalate dissolved methyl ethyl ketone peroxide chemical compound initiator MEKP-LA-3 (Peroxide Chemicals Ltd.) was used..

During the creation of composites, the purpose of carbon fiber reinforcement was to investigate the applicability of the high performance composite, while the use of a hybrid carbon and glass fiber reinforcing material was used to study the behavior of carbon-glass on the interface. For carbon fiber reinforced composites, I used PX35 UD 300 (Zoltek Zrt) type unidirectional (UD) carbon fiber (CF) with a nominal specific mass of 309 g / m².

For creating hybrid reinforcing compositions, WD 482/31 (Owens Corning Fiberglass Sprl) glass fiber (GF) UD fabric was added to the UD CF at a specific weight of 482 g / m². Between the used CF and GF reinforcements there is a significant specific weight difference. Since in this case I wanted to study the behaviour on the CF/GF interface, this did not have a particularly negative effect but this difference has been compensated by the layer build-up ([CF/CF/GF]_s) of the hybrid reinforced composites.

Production of investigated resin mixtures and composites

During my research I analysed mixtures of 75/25, 50/50 and 25/75 weight ratio of the three different two-component hybrid resin systems (EP / VE, EP / UP and UP / VE). Two different methods were used to produce these, the difference being in the mixing order of the ingredients and in mixing and setting times.

For the first method (signed #1 for resin samples, and “A” for composites), which is mentioned in the literature as a simultaneous method, I have taken into account the experiences of previous researches. During the process, the crosslinking of the resins forming the mixture is carried out simultaneously.

The second method (signed #2 for resin samples, and "B" for composites) was developed on the basis of a more rarely occurring sequential production method in the literature. During the process, the crosslinking of the resins forming the mixture takes place

in time. In the present case, one component is not completely crosslinked but pre-crosslinked when the second reaction is started.

The composite materials tested were made by hand-lay-up, which I applied to the UD fabrics in all cases in the same layer [0₆]. When using a hybrid reinforcement, the six layers of reinforcing material were laid in the same fibre direction, two layers of carbon (CF), two layers of glass (GF), and then again two layers of carbon fibre in the order [CF/CF/GF]_s. After the impregnation, the composite boards were pressed together with a Zwick Z050 loader between flat surface steel plates using a press frame to reduce the fluctuation in the thickness of the sheets.

Not all the hybrid resins tested were used for the composites. The reason for this was the mechanical strength of the VE/UP resins to demonstrate the full range produced in high performance CF reinforced composites. EP/UP and EP/VE resins had no strength improvement in comparison to the references, but with increased toughness, so I selected for composite producing the 50/50 # 1 and # 2 mixtures, which were also strengthened by CF and CF/GF. The reasons for selecting the given phase ratios for the EP/UP were excellent toughness and for EP/VE the mechanical properties of mixtures # 1 and # 2, which I wanted to study in composite.

Applied devices and testing methods

To measure the composition of resins and resin mixtures, I used RADWAG WXD 200/2000 digital scales with a measurement accuracy of 0.01 g in the range of 0 to 200 g. The mixing was carried out using a IKA RW-16 type stem mixer and a 29 mm diameter Appleton Woods ST3056 mixer at 240 rpm, which was determined by experiments to achieve the most efficient mixing. During the resuspension experiments, the samples were prepared by using a mold having a volume of 80 x 160 x 4 mm³ useful volume cavity. The 80 x 160 mm² side of the tool was held horizontally to fill the cavities and then clamped in this position between two flat glass plates using clamping hammers. The tool was held horizontally in a closed position at room temperature for 24 hours. From the finished sheets, I worked with the diamond-shaped cutter for the rectangular shaped 10 x 4 mm nominal cross-sectional specimens.

The samples to be tested were subjected to heat treatment after casting into the silicone mould and after laminating and pressing after 24 hours for subsequent curing. The heat treatment was carried out in a Heraeus UT20 laboratory air circulation oven at 80 ° C for a period of four hours. The heat treatment temperature was chosen above the nominal glass

transition temperature ($\sim 70^\circ\text{C}$) on the UP component data sheet, and the final temperature and duration were specified on the basis of preliminary experiments on the resin mixtures.

After compression, the composite laminates were heat-treated, as resin samples, for post-curing. The heat treatment was carried out in a Heraeus UT20 laboratory air circulation oven at 80°C for a period of four hours. During the heat treatment period, the composite sheets were stored between two plain steel sheets of the right size so that they could not be deformed during heat treatment.

From the pressed and heat-treated composite sheets, the specimens were fabricated using a diamond disc cutting machine parallel to the UD fibre direction (0°) and the perpendicular (90°) direction. During laser cutting, I used laser sighting.

Differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) were performed using a TA Instruments DSC Q2000 instrument according to MSZ EN ISO 11357-5: 2014. The temperature change in in situ curing test compounds was $10^\circ\text{C}/\text{min}$ for heating and a minimum cooling rate of $10^\circ\text{C}/\text{min}$ for heat/cool/heat cycle. In a modulated case of crosslinked samples, the temperature ranged from $3^\circ\text{C}/\text{min}$ to $\pm 0.5^\circ\text{C}$ with a 1-minute cyclic sinusoidal function in the range of 30 to 250°C in an inert atmosphere (50 ml/min, N_2).

During the resin experiments, a dynamic mechanical test (DMA) was performed for the structural analysis (10 x 4 x 55 mm) resin specimens according to ISO 6721-1: 2011. The measurements were performed on a TA-Instruments DMA Q800 Dynamic Mechanical Analyzer using a temperature effect of 20°C to 160°C with a $2^\circ\text{C}/\text{min}$ heating rate using a pure sinusoidal displacement excitation of 1 Hz with a minimum deflection of $5\ \mu\text{m}$ and $15\ \mu\text{m}$ amplitude, using a three-point bending load of 50 mm support..

Small angle neutron scattering (SANS) was performed on the KWS-1 low-angle diffractometer at the Heinz Maier-Leibnitz Zentrum FMR2 Research Reactor in Munich. During the measurements at room temperature at ambient air, the cold neutrons had a wavelength of $5\ \text{\AA}$ and the sample detectors were 8 to 20 m. The nominal size of the samples tested was 10 x 1 x 20 mm.

Fourier transformation infrared spectroscopy (FTIR) was performed using a Bruker TENSOR 37 type device with a diamond scan crystal, the brittle fractured surface of the specimens was scanned in attenuated total attenuated reflectance (ATR) mode in the mid infrared range in the 400 and $4000\ \text{cm}^{-1}$ wavelength spectra , Using 16 pastes for both the sample and the background.

Atomic force microscopy (AFM) tests were performed on a Nanosurf Flex AFM 5 in tapping mode. The required samples were prepared using Struers LaborPol-5 type polishing equipment with multi-stage polishing plates and finally with 1 μm slurry polishing. The polished samples were purified for 30 minutes in a Sonorex Super RK31 ultrasonic shaker bath in distilled water. When recording in phase contrast mode, the frequency of the free swing of the Tap190Al-G type tester used was approximately 155.6 kHz and 1024 x 1024 pixels were scanned during a scan interval of 1 second per line.

Surface hardness measurements were carried out on Zwick Roell HO4 3150, measuring 20 different points on each sample surface and evaluating their hardness value on ShoreD scale.

On the resin and the composite test pieces, the three-point bending test was performed on a Zwick Z020 type computer controlled universal loader. For resins, MSZ EN ISO 178: 2013, for composite test specimens according to MSZ EN ISO 14125: 2011, at room temperature. For the bending test, 4 x 10 x 80 mm specimens were used for resin samples and 15 x 2 x 100 mm nominal size specimens for composites. In all cases, I tested at least 5 specimens (in case of composites in the range of 0 and 90°), at a speed of 2 mm/min, 64 mm support distance for resin samples and 80 mm for the composites. The bending modulus of elasticity and deflections were calculated from the displacement of the crosshead of the machine.

The Charpy impact g tests were carried out according to MSZ EN ISO 179-2: 2012 on a CEAST Resil Impactor Junior impact rails at a support distance of 62 mm at room temperature, with a sample of 5 samples per material (for composites perpendicular to the sheets, in 0 and 90 °). The applied impact energy for resin samples were 2 J and 15 J for composites. During data capture, I applied DAS 8000 data processing unit. The ductility index of the composites (DI) was interpreted as the quotient of the amount of energy invested in the total fracture up to the maximum force that can be registered during the test.

The interlaminar shear tests (ILSS) were carried out in accordance with ASTM D3846: 08 (2015) using a compression load on specimens with standard parameters, which are from the composite sheets to the longest (0°) and perpendicular (90°). I examined at least 5 samples per material and fibre direction, with these diamond cutting discs dropped to the median plane of the laminates to cause the failure of the middle (symmetry) plane. The test is carried out on a Zwick Z020 universal computer controlled loader with a load speed of 1.3 mm/min, at room temperature, with the bending guard.

The fatigue tests were carried out on Instron 8872 computer-controlled universal loader according to ISO 13003: 2003 at room temperature with force-controlled three-point bending arrangement at pulsing load with 80 mm support distance and 10 Hz load frequency. The maximum load during cycles was determined at three different levels (load factor, LF), 85%, 90% and 95% of the average bending strength values obtained at static three-point bending tests, the minimum and maximum stress ratios, (R) was 0.1. For testing, 15 x 4 x 100 mm nominal size samples were used with 0 ° filament direction, at least 15 pieces per material type and per load level.

4. Summary

During my research I created mixtures of epoxy (EP), unsaturated polyester (UP) and vinyl ester (VE) polymer resins with two different simultaneous (#1) and one sequential (#2) production methods. From the resin mixtures, carbon and fiber-reinforced polymer matrix composites were prepared and tested for both the mixture resins and their composites.

In the first phase, I studied the effect of material combinations and the ratio of phase and method of production to the extent of the division of polymer mixtures. The samples were prepared using three different material combinations (EP/VE, EP/UP and VE/UP) at 75/25, 50/50 and 25/75 weight ratios. The choice of phase ratios was supported by thermodynamic calculations. Differential scanning calorimetry (DSC) studies during curing crosslinking of hybrids revealed that time-and-velocity differences between reactions of components could influence reaction-induced phase separation, thereby causing the phase structure to evolve. From DSC studies on cured resin samples, it was found that the three different pairs of exhibited a different degree of division of phases, causing a different size (weight) boundary phase connecting the two materials. In the EP/UP mixtures, a very large boundary phase was measured which resulted in a finer phase structure while the EP/VE combination was relatively highly phase-separated. The VE/UP system was located between the two blend groups with respect to the mass of the boundary phase. The Dynamic Mechanical Analysis (DMA) on the resin samples showed that the phase separation did not reach the level of two separate materials in the case of one of the tested resin mixtures, in which case a single glass transition temperature (T_g) could be registered. Based on the information provided by the low-angle neutron scattering and atomic force microscopic studies, it can be stated that nanostructured phase structure was produced in the hybrid resin systems produced. In the DMA studies, the storage modulus of the EP/UP and VE/UP blends exceeded the values of the reference substances due to the anti-plasticisation effect resulting

from interaction between the two phases and the hydrogen bonding between the two resins. The latter was verified by Fourier transformation infrared spectroscopy, but due to its low degree of modulation, the increase in modulus can be attributed to anti-plasticisation effect.

In the second phase of the work I examined the effect of the material pairing, the phase ratio and the production method on the mechanical properties of the hybrid resin mixtures. The results of the surface hardness test showed that VE/UP hybrid resins had higher hardness than VE and UP reference samples, and other samples belonging to the test pairs were of hardness among the references. This trend could also be established for three-point bending tests on susceptibility samples, where EP/UP and VE/UP resin pairing also showed a positive hybrid effect for the bending work required to break the specimens. The increase in bending work can be attributed, on the one hand, to the resulting fine phase structure and to the interaction between the components (hydrogen bonding, anti-plastering effect). In the case of Charpy impact tests, with few exceptions, all hybrid materials showed higher impact strength than the reference materials. This means that the resulting fine phase structure did not have a negative effect on the strength and modulus of the materials, but was able to increase their toughness. For the tested resin mixtures, both the #1 and #2 production methods are suitable for the production of a high strength composite matrix material. As regards the phase ratio, the results of mixtures of 50/50 are most favourable in the EP/VE and EP/UP combinations for the mechanical properties of the matrix materials created. VE/UP blends had good mechanical properties with all three ratios applied, so it is worth examining their composites.

In the third phase of the work, three different phase ratios (75/25, 50/50 and 25/75) using VE/UP mixtures using two different methods (# 1 and # 2) were used to produce (UD) carbon fibre composites for investigating their phase effect. In addition, composite materials with UD hybrid carbon/glass (CF/GF) amplifier were prepared using the 50/50 phase (EP/VE and EP/UP) mixtures using the 50/50 weight ratio mix with # 1 and # 2 method, for investigating the properties of hybrids in the CF / GF phase boundary. In order to analyse its behaviour. UD CF was used to create composites with a similar EP/VE and EP/UP hybrid matrix.

New scientific results:

1st thesis: Two-component, (bisphenol A diglycidyl ether-based) epoxy/(orthophthalic acid-based) unsaturated polyester and (bisphenol A bis-methacrylate-based) vinyl ester/(orthophthalic acid-based) unsaturated polyester hybrid resin systems can have the highest strength and toughness compared to the reference samples if the mass of the cross-phase in the phase structure resulting from crosslinking is comparable to the mass of the other two phases of the system. The reason for this is that the boundary phase provides an excellent link between the two other phases, and this phase structure also facilitates the anti-plasticisation of the hybrid resin.

2nd thesis: By the hybridisation of bisphenol-A-methacrylate-based vinyl ester (VE) and orthophthalic acid-based unsaturated polyester (UP) polymer resins, a resin mixture can be produced which has greater bending strength and bending work than the VE or UP component of the mixture. This is due to the fact that the VE/UP mixture has a nanostructured phase structure that promotes co-operation between the two components and in which hydrogen bonds can be found between the two components [1].

3rd thesis: A significant, 5-20% increase can be achieved in the interlaminar shear strength of carbon and carbon/glass fibre reinforced composites if they are made with EP/VE, EP/UP and VE/UP hybrid polymer resin systems as matrix, prepared from bisphenol-A-diglycidyl-ether-based epoxy (EP), bisphenol-A-methacrylate-based vinyl ester (VE) and orthophthalic acid-based unsaturated polyester (UP). This is due to the fact that hybrid resin systems behave more ductilely than the references that inhibit the spread of cracks, thus increasing the energy demand of the cracking process [2-4].

4th thesis: Polymer composites with carbon fibre and carbon/glass hybrid reinforcement, prepared with a hybrid matrix with a 1:1 weight ratio, of (bisphenol-A-diglycidyl-ether) epoxy and (bisphenol-A-methacrylate) vinyl ester polymer resins can have a significantly longer (50% to 350%) lifetime in the case of three-point bending fatigue tests, at 0.90 and 0.85 load levels than composites with a non-hybrid matrix. This is due to the fact that the nanostructured phase structure of the matrix material can have a higher degree of energy absorption, thus inhibiting the formation and spread of cracks in the matrix during repetitive stresses [2, 5-8].

5th thesis: In the cyclic bending wear of (bisphenol-A-diglycidyl-ether-based) epoxy, (orthophthalic acid based) unsaturated polyester and (bisphenol-A-bis-methacrylate based) vinyl ester matrix composites, the failure process (which causes a decrease in modulus) can be fully described more easily, with fewer parameters, with the transposed delayed logistic function completed with a correction element, than with formulae used so far in the literature:

$$E_R/E_0 = 1 - b \left(\frac{1}{n/N} - 1 \right)^{-\frac{1}{a}} + m,$$

where E_R/E_0 is the quotient of the remaining and the initial modulus of elasticity, n/N is the quotient of the actual and the failure load cycle count, b is the inflection point of the curve, i.e. the degree of relative modulus decrease at the start of crack propagation, and a is the failure rate control parameter. The correction element m is related to the degree of modulus decrease in the first phase of failure.

5. List of own publications

- [1] Horváth K., **Turcsán T.**, Mészáros L.: *A fázisarány hatása hibrid polimer rendszerek esetén*. OGÉT, XXIV. Nemzetközi Gépészeti Találkozó, conference proceedings , 210–213 (2016).
- [2] **Turcsán T.**, Mészáros L.: *Mechanical performance of hybrid thermoset composites: Effects of matrix and reinforcement hybridization*. Composites Science and Technology, **141**, 32–39 (2017). **IF:3.897**
- [3] **Turcsán T.**, Mészáros L.: *Nanostructured Polymer Matrix Composites for High Performance Engineering Applications*. Nanotech France 2015, International Conference, Paris, France, June 15-17, conference proceedings, 69–70 (2015).
- [4] **Turcsán T.**, Mészáros L.: *Hybrid Thermoset Matrix Carbon Fibre Reinforced Composites, a Study of Interlaminar Properties*. Materials Science Forum, **885**, 309–313 (2017).
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- [6] **Turcsán T.**, Mészáros L.: *Nanostrukturált mátrixú kompozitok, az anyagfejlesztés új irányzata*. Polimerek, **2**, 109–111 (2016).
- [7] **Turcsán T.**, Mészáros L.: *Development of high performance fiber reinforced polymer composite with toughened matrix*. The Fiber Society Spring 2014, Technical Conference, Liberec, Czech Republic, May 21–23., conference proceedings 69–71 (2014).
- [8] **Turcsán T.**: *Növelt energiaelnyelő képességű kompozitok fejlesztése*. GÉP periodicals, **64**, 58–61 (2013).