

Mechanical performance of hybrid thermoset composites: Effects of matrix and reinforcement hybridization

Turcsán T., Mészáros L.

This accepted author manuscript is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and MTA. The definitive version of the text was subsequently published in [Composites Science and Technology, 141, 2017, DOI: [10.1016/j.compscitech.2017.01.005](https://doi.org/10.1016/j.compscitech.2017.01.005)]. Available under license CC-BY-NC-ND.

Mechanical performance of hybrid thermoset composites: Effects of matrix and reinforcement hybridization

Tamas Turcsan^{1,*}, Laszlo Meszaros^{1,2}

1: Budapest University of Technology and Economics, Department of Polymer Engineering, Muegyetem rkp. 3., H-1111 Budapest, Hungary

2: MTA–BME Research Group for Composite Science and Technology, Muegyetem rkp. 3., H-1111 Budapest, Hungary

*corresponding author, e-mail: turcsan@pt.bme.hu

Abstract

Hybrid epoxy/vinyl ester (EP/VE) and epoxy/unsaturated polyester (EP/UP) resins were used as matrices to prepare unidirectional carbon fibre (CF) and carbon/glass fibre (CF/GF) reinforced composites targeting toughness of improvement. Hybrid resins were produced simultaneously (one-pot) and sequentially. (Thermo)mechanical properties of hybrid resins were determined in surface hardness, three-point bending, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC) tests. Hybrid matrix composites with CF and CF/GF hybrid reinforcements were characterized with quasi-static mechanical (three-point bending) tests performed in 0° (longitudinal) and 90° (transverse) directions. In addition, flexural fatigue tests were run on UD composites. Interlaminar properties were deduced from in-plane shear strength (IPSS) test and fractographic inspection in a scanning electron microscope. The EP/VE hybrid resin exhibited improved energy absorption compared to neat constituent resins in contrast to EP/UP. Using hybrid resins as matrix highly improved the toughness and durability of the corresponding composites. Improved energy absorption was attributed to the phase structure of the hybrid resins, which also positively affected the IPSS.

Keywords: A. Carbon fibre, A. Glass fibres, B. Fatigue, B. Mechanical properties, IPN

1. Introduction

Fibre-reinforced polymer composites (FRPCs) have been greatly improved since they were first used in the middle of the 20th century. In the last few decades, FRPCs with enhanced properties have been developed to satisfy industrial demands [1]. One of the most important requirements besides high strength and modulus is toughness and mechanical durability. It is a challenge in the case of relatively brittle thermoset matrix FRPCs compared to ductile plastics, metals and alloys [2]. Hybrid resins as matrix material could be a feasible solution for this problem in cases where the relatively tough but limited strength thermoplastic polymer composites cannot be used. The special morphological structure of hybrid resins, widely called interpenetrating polymer network (IPN), increases the damping properties of composites, due to the entangled phases of the mixed resin. Because of phase conformation, this hybrid material can react differently to mechanical and thermo-mechanical loads compared to non-hybrid resins. The properties and possibilities of IPNs compared to neat resins have been investigated since the second half of the previous century [3-5]. The characterization of the formation of the network and thermo-mechanical proof of the phase structure have been published [5-8]. Numerous favourable attributes, for example enhanced damping properties [9-12], have been discovered and extensively analysed. Several kinds of polymer resin pairs were investigated, such as epoxy (EP) with polyurethanes (PU) [9, 13-15], EP with unsaturated polyester (UP) [10, 16], PU with UP resin [17, 18], and EP with vinyl ester (VE) resin [11, 19, 20]. Hybrid resins have great damping abilities and some of them also showed synergistic mechanical properties. In addition, the hybridization of thermoset resins combines some of their favourable properties, for example good mechanical properties and the solvent-free processing of EP, excellent chemical resistance of VE, and the

relatively affordable price of UP. Because of the increased damping abilities, hybrid resins could be a feasible matrix material of FRPCs. Although these hybrid materials composed of at least two resins have been in use for decades, their application as composite matrix is not common and has not been well published so far. FRPCs with a hybrid matrix have been investigated [21, 22], but they focused mostly on the effect of surface treatment of the fibres and its impact on mechanical properties. Moreover, these studies used almost exclusively basalt and glass fibres (GF). Few papers have examined high-performance carbon fibre (CF) reinforced hybrid resin matrix composites and their morphological and mechanical properties [23]. In short, much could be done to improve the toughness and durability of FRPCs with a hybrid resin matrix. On the other hand, hybridization of the reinforcement is a keenly investigated subject in the case of thermoplastic [24, 25] and thermoset matrix FRPCs [26-33]. These studies mainly focused on the enhancement of mechanical properties of thermoset matrix FRPCs but hybrid reinforcement also resulted in improved energy absorption and reduced delamination. Several types of reinforcement (mostly CF and GF) layers were used in different structural compositions. Combining hybrid matrix materials with hybrid reinforcement can result in even better properties. Therefore, this study investigates the effect of matrix and reinforcement hybridization in the case of thermoset FRPCs. The aim of this paper is also to investigate the toughening effect of EP/VE and EP/UP hybrids as matrix material. The EP/VE and EP/UP combinations were chosen because of the reduced styrene content compared to the neat UP and VE, and the reduced price compared to the initial EP. This study also examines the mechanical properties of hybrid resin matrix-hybrid CF/GF reinforced composites from a mechanical properties point of view.

2. Materials

A diglycidyl ether of bisphenol A type resin was used as EP with 188 g/epoxy equivalent and a density of 1.17g/cm³ (IpoX ER 1010, IpoX Chemicals, Hungary). Its hardener was isophorone diamine, with 43 g/hydroxy equivalent and ~660 mg KOH/g amine value (IpoX EH 2293, IpoX Chemicals, Hungary). An orthophthalic acid-based resin with 39-42% styrene content was used as UP (DISTITRON-5119-ESX20ZQ, Polynt S.p.A., Argentina). A bisphenol-based resin with 35% styrene content was used as VE (AME 6000 T 35, Ashland S.p.A., Italy). The UP and VE resins were accelerated with 2 wt% methyl-ethyl ketone peroxide dissolved in diisobutyl phthalate (MEKP-LA-3, Peroxide Chem., South Africa).

Unidirectional (thin polyester yarn-stitched) carbon plies were used, with an areal weight of 309 g/m² CF in 0° and 10 g/m² GF in 90° directed rovings (PX35 UD300, Zoltek, Hungary). Carbon fibres of UD plies were sized for EP and VE and had a diameter of 8.3±0.9 µm, a tensile strength of 2.48±0.49 GPa and a tensile modulus of 133.5±17.5 GPa. UD (thin glass filament-stitched) glass plies were used with an areal weight of 482 g/m² in 0° and 31 g/m² in 90° GF rovings (WR 482/31, Owens, Belgium). Fibres in the GF plies were sized for EP, UP and VE and had a diameter of 17.1±2.9 µm, a tensile strength of 1.46±0.70 GPa and a tensile modulus of 54.69±9.07 GPa.

3. Experimental

3.1. Sample production and preparation

Based on previous investigations [7, 8, 19, 23], 1:1 weight ratio mixed hybrid resins and two different procedures of mixing were used. One of them, called the simultaneous or one-pot method (henceforth referred to as method 'A'), was described in detail in former publications [19, 23]. Another method called sequential-like process (henceforth referred

to as method 'B') was based on former studies [5]. The first step of the sequential-like method was the mixing of EP with its amine hardener for two minutes. Then the compound had a dwelling time of 30 minutes at 25°C without stirring. After dwelling, the second resin (UP or VE) was added to the pre-reacted EP and stirred for two minutes. Then the curing agent of the second resin was added and stirred for two minutes again.

Resin samples were created with silicone moulds with a cross section of 4mm x 10 mm. After moulding, specimens were kept in the mould at room temperature for 24 hours. Composites were made by hand lay-up. 6 layers of unidirectional plies oriented in the same direction were used for CF and CF/GF reinforced composite specimens. The latter consisted of two outer CF "belts" (2 layers each) and an inner part of two GF layers. The benefits of this construction are low estimated decrease of stiffness and strength due to the CF "belts", and expected energy absorption caused by the GF "core". With this construction the coupling ability of hybrid resins at the CF/GF phase boundary can be observed (**Fig 1**). Besides hybrid matrix composites, reference samples with identical reinforcement orientation and content were also prepared from plain EP, UP and VE resins. The designations of the materials, the resin content of the matrix, the layer build-up and the volume fraction of fibres are described in **Table 1**. The designation, mixing method and resin contents apply to resins and composites as well. The differences between the volumetric fibre content of CF and CF/GF reinforced composites may be an effect of the larger interfibre space between the glass (larger diameter) than the carbon (smaller diameter) fibres, which resulted in higher resin uptake in the case of GF.

After the hand lay-up process, laminates were pressed in a 2.00 ± 0.05 mm thick steel frame, between parallel steel plates with a hydraulic press with 0.5 MPa compressive stress at room temperature for 24 hours. After silicone moulding and pressing, resin

samples and composite plates were cured at 80°C for 4 hours. The composite specimens for mechanical tests were cut out in two different directions. In the first group the longer side was parallel to the UD fibres (henceforth referred to as 0°), whereas in the other group the longer side was normal to the direction of the fibres (henceforth referred to as 90°). For all investigations at least five (except fatigue, where fifteen) specimens were used for each material type and load case.

3.2. Thermal and thermomechanical characterization of resins

The DMA test was carried out on a Q800 (TA Instruments, USA) device, according to ISO 6721-1:2011, in three-point bending mode, at a load frequency of 1 Hz, in strain actuation mode, with a 55 mm x 10 mm x 4 mm specimen size, 50 mm span length, a temperature range of 20°C to 150°C and a heating rate of 2°C/min. DSC investigations were carried out on a Q 2000 device (TA Instruments, USA) according to ISO 11357-5:2014, on a 8 mg sample with a 10°C/min heating ramp, and a temperature range of 30°C to 210°C in a N₂ atmosphere.

3.3. Mechanical characterization

The surface hardness of resin samples was measured on the Shore D scale with a Zwick Roell HO4 3150 hardness tester, at room temperature at 20 different points on the surface.

Flexural properties were measured according to ISO 178:2013 (for resins) and according to ISO 14125:2011 (for composites). Flexural tests were carried out on a Zwick Z020 (Germany) universal testing machine, at a test speed of 2 mm/min, a span length of 64 mm, and a cross section of 10 mm x 4 mm (resins), and a span length of 80 mm, and a cross section of 15 mm x 2 mm (composites). Flexural tests were also carried out for samples with reinforcement oriented at 0° (longitudinal) and 90° (transversal) (**Fig 1**). In

the case of 0° samples the reinforcing effect of the fibres, and in the case of 90° samples the behaviour of the matrix can be better investigated.

In-plane shear strength (IPSS) tests were carried out in compressive mode, at a test speed of 1.3 mm/min on a Zwick Z020 (Germany) universal testing machine at room temperature according to ASTM D3846:08(2015). The IPSS specimens were double-side notched to the middle layer. To avoid buckling, standardized adapter was used.

Fatigue of 0° composites were characterized on an Instron 8872 (USA) fatigue testing machine in flexural mode (three-point bending) at room temperature, with 100 mm x 15 mm x 2 mm test specimens, a span length of 80 mm, according to ISO 13003, in force-controlled mode, with load factor (LF) values of 0.85, 0.90 and 0.95, 0.1 stress ratio (R) and at a loading frequency of 10 Hz.

3.4. Surface morphology and the determination of fibre content

ILSS fracture surfaces were examined with a JEOL JSM 6380LA (Japan) scanning electron microscope (SEM) in secondary electron imaging mode. To avoid overcharging, samples were coated with a thin Au layer. The fibre content of composites was determined by ashing the samples (ISO 3451-1:2008) in an atmosphere of air at 500°C for 1 hour. The oxidation of CF was measured separately with a Q2000 TGA device (TA Instruments, USA) and ashing results were corrected with the ~2m% weight loss of CF.

4. Results and discussion

4.1. Characterization of resin samples

A DSC analysis of EP/VE hybrid resin systems (**Fig 2**) showed more than one glass transition temperature (T_g) in the case of both mixing methods. The lower T_g of A and B hybrid (97 and 95 °C) belongs to the EP rich phase, while the higher ones (119 and 127°C)

to the higher (129°C) T_g VE rich phase of the mix. The DMA results of the EP/VE system showed only one transition temperature and it matched one of the T_g -s obtained with the DSC analysis. In the case of EP/VE/A the T_g was the lower (88°C) T_g , while in the case of EP/VE/B it was the higher (121°C) T_g determined with the DSC analysis. EP/VE/A, where the phase with 88°C T_g was dominant, had a similar storage modulus to EP, while EP/VE/B, where the higher T_g phase was dominant, had a higher storage modulus than similar to VE resins at room temperature. The tan delta curves of EP/VE hybrids (**Fig 3/a**) showed a relatively wide glass transition temperature range (because of the superposition of phase-separated components), but the level of phase separation was not significant enough to influence mechanical properties, therefore DMA tests resulted in only one peak. Tan delta values of hybrids were unambiguously higher than those of neat resins, which can be attributed to the increased damping abilities of EP/VE hybrids.

EP/UP systems showed single T_g -s and higher tan delta peaks than their parent resins (**Fig 2 and 3/b**). Transition temperatures obtained with DSC and DMA tests were similar in the case of EP/UP hybrids and were between the EP and the UP T_g values. It is according to IPN definition and probably means a relatively low level of phase separation. Storage modulus values showed the same tendency as the storage modulus values of the EP/VE system. Tan delta curves were very similar in the case of EP/UP/A and EP/UP/B, which means similarity in the phase structure of one-pot and sequentially made hybrids. The compatibilization of hybrid resins might have occurred through grafting reactions between the epoxy and secondary hydroxyl groups of VE in the case of EP/VE, and hydroxyl and carboxyl groups of UP in the case of EP/UP. In fact, the chemical structure of the EP, and even its hardeners, may affect the outcome of hybridization (see [35].) but this effect is beyond the scope of the present work.

The results of flexural and surface hardness tests (**Fig 4**) showed that the surface hardness of EP/VE and EP/UP hybrids was between the surface hardness of the neat components. EP/VE/A and B hybrids had 16% and 9% higher specific flexural work (w_f) than the average value of references, calculated with equation (1):

$$w_f = \int_0^D F d\delta / (b \cdot d) \quad (1)$$

where D is the ultimate deflection of the specimen, δ is the deflection, F is the flexural load, and b and d are the width and the thickness of the cross-section. The w_f is related to the energy absorption and toughness of the resins. The 16% and 15% improvements in w_f and flexural strength (σ_f) of the EP/VE system produced by method A can be attributed to the formerly mentioned synergistic IPN properties. Additional toughness or strength arise from the entangled chains (more exactly phases) of the resins. The entangled phases may yield enhanced stiffness and strength through the related “mechanical interlocking”. In addition, their large surface area supports van der Waal's interactions. Grafting, which is an even more efficient “booster” of strength and stiffness, may be at work in the case of EP/VE/A. The effect of chemical grafting between the phases, however, seems to be rather low because neither T_g nor σ_f or hardness was enhanced.

In the case of the EP/UP system hybridization resulted in no improvement of strength or toughness in spite of a single T_g , which refers to a good level of compatibility. Hybridization may allow more flexible deformation besides an acceptable level of strength compared to neat resins. EP/UP/A had similar σ_f values to those of EP and EP/UP/B had similar σ_f values to those of UP, which shows the dominant resin in the hybrid, as can be seen in the results of storage modulus in **Fig 4**.

4.2. Three-point bending of composites

The longitudinal (0°) load direction:

Out of CF reinforced composites (**Fig 5/a**), neat VE matrix composites had higher σ_f than EP matrix composites, but both showed higher σ_f and E_f than UP matrix composites. Using an EP/VE hybrid matrix resulted in 15.5% and 10.8% higher σ_f compared to references, in case of A and B preparation route of the hybrid resin respectively. This is because EP/VE hybrids already had higher energy absorption as a resin, which also remained when they were used as a matrix. On the other hand, CF fibres were sized for EP and VE and this resulted in good adhesion at the phase boundary. The E_f and D values of these composites were between those of their references. The σ_f values of EP/UP matrix composites were between those of their references but higher D and lower E_f were detected, irrespective of the preparation route of the hybrid. EP/UP hybrids had similar mechanical properties to those of their parents in resin flexural tests, but as composites, they showed additional flexibility. It can be attributed, on one hand to the main properties of the UP component and on the other hand to matrix-fibre connection, because CF was not sized for UP.

The CF/GF hybrid reinforcement in the 0° load case (**Fig 5/b**) resulted in $32 \pm 0.1\%$ lower σ_f values compared to CF reinforced composites. It can be attributed to differences in volumetric fibre content (**Table 1**) and also to the lower strength of GF. On the other hand, strength differences between CF and CF/GF reinforced systems are due to differences in the failure modes of the related composites. In the case of CF reinforcement, failure was detected in the layers under tension in the form of fractures. In the case of CF/GF, failure occurred as delamination in the CF/GF phase boundary layer under tension, which was usually accompanied by undulation in the CF layers under

compression. Of the CF/GF reinforced neat resin matrix composites, EP matrix composites showed the highest σ_f , VE the highest E_f values, and UP exhibited the worst properties. CF/GF reinforced EP/VE hybrids showed no significant improvement compared to references. The σ_f and D values of EP/VE matrix composites were similar to those of their references but their E_f was 12% lower in case of A and 21% lower in case of B method prepared matrix. It means some additional flexibility besides a good level of strength which can be attributed to the phase structure of EP/VE hybrids. Using an EP/UP hybrid matrix had a positive impact on D but not on σ_f and E_f . The CF/GF reinforced EP/UP hybrids had E_f and σ_f values close to those of the UP matrix references. The reason is poor fibre matrix adhesion between UP and CF. EP/UP/A had a drastically lower E_f than EP/UP/B, which means a poor level of fibre matrix adhesion in this case, especially at CF “belts”. High D values without failure can be traced back to the non-grafted but entangled phase structure of EP/UP hybrid resins, which allowed more flexibility and resulted in delayed crack spreading in the matrix.

The transversal (90°) load direction:

Out of CF reinforced references (**Fig 6/a**) EP matrix composites showed the highest strength (69.2 MPa), VE matrix composites had the best E_f values (10.2 GPa), and UP matrix composites had the lowest strength and moduli. EP/VE matrix composites had a positive hybrid effect; they showed at least as high a σ_f as EP matrix composites but also a relatively high modulus (9.3 and 10.9 GPa) like the VE matrix reference. The EP/VE/A matrix composites had the highest σ_f (77.2 MPa) but lower E_f compared to EP/VE/B. Both of them had lower D values compared to references. This explains the formerly mentioned additional flexibility besides a good level of strength. This is in accordance with the results of resin flexural tests (**Fig 4**), where the EP/VE system resulted in a good level of

strength and outstanding energy absorption. The CF reinforced EP/UP/A matrix composite showed a σ_f which is the average of that of the references, and the σ_f of the EP/UP/B system is almost as high as that of the EP matrix. The E_f and D values are similar to those of the references. In this case, the behaviour of the matrix was dominant and EP/UP matrix composites had 47% and 77% strength improvement compared to UP matrix reference because of the IPN structure.

CF/GF reinforced composites (**Fig 6/b**) had less worsening of the properties in this load case compared to CF reinforcement composites (**Fig 6/a**). Among neat resin matrices CF/GF composites showed less difference in mechanical properties than in the 0° load case. A hybrid matrix with hybrid reinforcement had improved σ_f in all cases. The EP/VE/A matrix composite showed the highest strength and similar E_f and D values to VE. The E_f and D of EP/VE/B were the same as those of EP matrix composites. This trend can be observed in the case of several kinds of reinforcements and load and probably points to the dominant resin in the hybrid. The EP/UP hybrid resin resulted in higher D and significantly improved σ_f but lower E_f values this load case. Methods A and B produced matrices which resulted in similar E_f and D values, but EP/UP/A showed a higher σ_f . This phenomenon can be attributed to the above-mentioned additional flexibility of the IPN structure and in this case there was also good adhesion between UP/GF and EP/CF. Overall, better coupling is observed at the phase boundary. Another explanation is that this load case (i.e. 90°) resulted in lower stress “jumps” at the CF/GF phase boundary compared to the 0° load case (see sketches in **Fig 1**). Hybrid matrices may better connect the GF/CF phase boundary thereby preventing crack propagation because of their higher ductility compared to the plain resins.

4.3. In-plane shear strength of composites

The type of reinforcement did not influence IPSS as much as in the case of 0° flexural tests (**Fig 7**). Of CF reinforced neat resin matrix composites, EP showed the highest shear strength followed by VE and UP (**Fig 7/b**). EP/VE hybrids showed 17-21% in-plane shear strength (τ_{IPSS}) improvement compared to the references, and EP/UP hybrids had similar values to EP in both cases, irrespective of the preparation method. The reason for this phenomenon is that the phase structure allowed made hybrid matrices more ductile and tougher, which can be seen in the SEM fracture surface micrographs of IPSS specimens (**Fig 8**). Fracture surfaces showed a parallel shearing effect, but cracking mechanisms were different in the case of CF reinforced neat (**Fig 8/a-c**) and hybrid matrix composites (**Fig 8/d-g**). The surface of the latter was partitioned, shell-like, and exhibited hackle pattern [30, 36] formations. This phenomenon required a lot of energy during cracking, which caused higher IPSS for hybrid matrices.

CF/GF reinforced composites showed 13% lower strength in the case of EP and 45% lower strength in the case of the VE matrix compared to CF reinforced composites. In this case GF layers were sheared and decreased strength can be attributed to the worse interaction of GF/EP and GF/VE (**Fig 8/a** and **/b**). A 18% strength decrement can be observed in the case of the EP/VE/CF/GF system, but a 5.5% improvement in strength in the case of EP/UP/A/CF/GF and 31% in case of EP/UP/B/CF/GF. This effect can be caused by the above-mentioned worse fibre-matrix connection, which was balanced by the better toughness of the hybrid resin. The reason for the latter effect can be the additional flexibility caused by the IPN, similarly to the flexural test, especially in the 90°load case, in addition to the relatively good UP/GF connection. The fracture surface of CF/GF composites was similar to that of CF reinforced composites (**Fig 8**). In the

sheared cross-section, among the larger diameter GF fibres, thinner but deeper hackle patterns can be observed. These resulted in a deformed surface and energy demand in the case of Gf reinforced hybrid resins similarly to CF reinforced hybrid resins.

4.4. Flexural fatigue tests of composites

In the case of a neat resin matrix and CF reinforcement (**Fig 9/a**), EP/CF showed the highest abided cycle numbers followed by VE and UP, at all LFs. The EP/VE matrix resulted in 56% and 40% higher mechanical durability at LF 0.85 and 48% and 6% at LF 0.90 than the average of their references, in case of A and B production method of the hybrid resin respectively. The reason is that the IPN phase structure allowed improved toughness, which was shown in resin flexural tests (**Fig 4**) and proper fibre-matrix connection, which was mentioned at composite flexural tests (**Fig 5/a**). A and B method hybridization of EP/UP resulted in 89 and 85% improvement in mechanical durability compared to the average of their references the case of CF reinforcement at 0.85 LF. The improvement is clear (47 to 78%) at 0.90 and 0.95 load factors as well. The reason for this phenomenon is that the EP/UP matrix was less rigid even in the case of quasi-static flexural tests. This toughness comes from the phase structure of the hybrid resin, which allowed high energy absorption. The EP/UP/A resulted in better durability compared to EP/UP/B; it can be attributed to the better toughness, namely the higher w_f of it (**Fig 4**).

CF/GF reinforced neat resin matrix materials (**Fig 9/b**) had a similar tendency but smaller differences compared to CF reinforcement and at 0.95 LF neat VE showed the highest cycle numbers. Hybrid reinforcement had an impact on durability and resulted in lower cycle numbers at 0.85, similar numbers at 0.90 and higher cycle numbers at 0.95 LF compared to CF reinforced composites. The reason for lower numbers at 0.85 LF is that the phase boundary between CF and GF layers is not “coupled” properly and this is

probably shown in the corresponding stress-strain behaviour. This causes delamination and results in early fracture in the compressed CF/GF phase boundary. In the case of LFs 0.90 and 0.95 the energy absorbing ability of GF “core” manifested itself and caused improvement compared to neat resin matrix composites with only CF reinforcement. If the resin showed a proper level of strength and toughness simultaneously in quasi-static tests, it was able to couple the CF/GF phases properly, and this resulted in an increment of durability at 0.95 LF compared to CF reinforcement. EP/VE/CF/GF hybrids were of this type and resulted in averagely 58.5 and 17.1% improvement (in case of A and B method prepared hybrids respectively) in number of cyclic loads compared to CF/GF references at all LFs. This can be attributed to the above-mentioned good flexural properties of EP/VE resins (**Fig 4**) and their composites (**Fig 5/b**). The explanation of the better durability of EP/VE/A compared to the EP/VE /B type CF/GF composites is the better energy absorption, which could be seen in the resin flexural test (w_f , in **Fig 4**). The EP/UP matrix with CF/GF reinforcement did not have better durability than either the same matrix with CF reinforcement or its references. The reason for this is the low static flexural strength and moduli of EP/UP/CF/GF composites (**Fig 5/b**).

5. Conclusions

Based on this study it can be concluded that the hybridization of epoxy and vinyl ester is a good way to increase the toughness of thermoset resins without sacrificing their strength. This improvement in toughness can be explained with the entangled phase structure, which resulted in a higher area of the phase boundary and additional flexibility, and this led to better energy absorption. DMA and DSC tests on the hybrid resins showed that phase separation of constituent resins was higher in the case of EP/VE than in the case of EP/UP, irrespective of their method of preparation (simultaneous or sequential).

The EP/VE hybrid matrix showed increased damping and energy absorbing abilities as a resin compared to neat EP and VE resins, as shown in the mechanical and (thermo)mechanical tests. This positive change in properties can be observed if EP/VE resins are used as composite matrix. Besides CF and CF/GF reinforcement, the EP/VE hybrid matrix resulted in improved strength and interlaminar properties. CF fibres caused better mechanical durability, but CF/GF reinforcement did not result in any improvement of transverse flexural and interlaminar properties compared to constitute resin matrix composites. EP/UP hybrids as a resin did not have increased energy absorption, but using them as matrix also resulted in an improvement in mechanical properties, especially in the case of transverse flexural tests. Hybrid matrix in case of both reinforcements (CF and CF/GF) showed better interlaminar properties compared to neat resin matrix composites, but CF reinforcement resulted in high mechanical durability in EP/UP hybrids.

The toughening effect of hybrid matrices is a useful way to increase the mechanical durability of CF reinforced composites. The interlaminar properties of CF/GF hybrid reinforcement can be enhanced with an EP/VE or EP/UP hybrid matrix.

Acknowledgement

This research was supported by TÁMOP 4.2.4.A/1-11-1-2012-0001 „National Excellence Program”, the Hungarian Research Fund (OTKA PD105564) and the Janos Bolyai Research Scholarship of the Hungarian Academy of Sciences.

References

- [1] Peters ST. Handbook of composites. Springer US, 1998.
- [2] Sabu T, Kuruvilla J, Malhorta SK, Goda K, Sreekala MS. Polymer composites, volume 1, Macro- and microcomposites. Wiley-VCH, 2012.
- [3] Sperling LH, Interpenetrating Polymer Networks and Related Materials, New York: Springer US, 1981.

- [4] Lipatov YS. Phase-separated interpenetrating polymer networks, Berlin, Heidelberg: Springer-Verlag, 2007.
- [5] Ignat L, Stanciu A. Advanced Polymers: Interpenetrating. In: Kulshreshtha AK, Vasile C, editors. Handbook of Polymer Blends and Composites. Shrewsbury: Rapra Technology, 2002,. p.275-329.
- [6] Kim S C, Klempner D, Frisch KS, Radigan W, Frisch HL. Polyurethane Interpenetrating Polymer Networks I., Synthesis and Morphology of Polyurethane-Poly(methyl methacrylate) Interpenetrating Polymer Networks, *Macromolecules* 1976;9(2):258-263.
- [7] Gryshchuk O, Karger-Kocsis J. Nanostructure in Hybrid Thermosets with Interpenetrating Networks and its Effect on Properties. *J Nanosci Nanotechno* 2006;6(2):1-7.
- [8] Karger-Kocsis J, Gryshchuk O, Schmitt S. Vinylester/epoxy-based thermosets of interpenetrating network structure: An atomic force microscopic study. *J Mater Sci* 2003;38(3):413-420.
- [9] Chern YC, Tseng SM, Hsieh KH. Damping properties of interpenetrating polymer networks of polyurethane-modified epoxy and polyurethanes. *J Appl Polym Sci* 1999;74(2):328-335.
- [10] Lin MS, Liu CC, Lee CT. Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy. *J Appl Polym Sci* 1999;72(4):585-592.
- [11] Karger-Kocsis J, Gryshchuk O, Jost N. Toughness response of vinylester/epoxy-based thermosets of interpenetrating network structure as a function of the epoxy resin formulation: effects of the cyclohexylene linkage. *J Appl Polym Sci* 2003;88(1):21-24.
- [12] Chen S, Wang Q, Wang T. Damping, thermal, and mechanical properties of carbon nanotubes modified castor oil-based polyurethane/epoxy interpenetrating polymer network composites. *Mater Design* 2012;38:47-52.
- [13] Cascaval CN, Ciobanu DC, Rosu D, Rosu L. Polyurethane-epoxy maleate of bisphenol a semi-interpenetrating polymer netw. *J Appl Polym Sci* 2002;83(1):138-144.

- [14] Hsieh KH, Han JL, Yu C, Fu S. Graft interpenetrating polymer networks of urethane-modified bismaleimide and epoxy (I). *Polymer* 2001;42(6):2491-2500.
- [15] Park SJ, Jin JS. Energetic studies on epoxy–polyurethane interpenetrating polymer networks. *J Appl Polym Sci.* 2001;82(3):775-780.
- [16] Ivankovic M, Dzodan N, Brnardic I, Mencer HJ. DSC study on simultaneous interpenetrating polymer network formation of epoxy resin and unsaturated polyester. *J Appl Polym Sci* 2002;83(12):2680-2698.
- [17] Hsu TJ, Lee J L. Processing of polyurethane–polyester interpenetrating polymer network (IPN). *J Appl Polym Sci* 1988;36(5):1157-1176.
- [18] Meyer GC, Mehrenberger PY. Polyester-polyurethane interpenetrating networks. *Eur Polym J* 1977;13(5):383-386.
- [19] Karger-Kocsis J. Simultaneous interpenetrating network structured vinylester/epoxy hybrids and their use in composites. In: Harrats C editor. *Micro- and Nanostructured Multiphase Polymer Blend Systems*. Boca Raton: CRC Press, 2005.
- [20] Dean K, Cook WD, Zipper MD, Burchill P. Curing behaviour of IPNs formed from model VERs and epoxy systems I.: amine cured epoxy. *Polymer* 2001;42(4):1345-1359.
- [21] Czigany T, Poloskei K, Karger-Kocsis J. Fracture and failure behavior of basalt fiber mat-reinforced vinylester/epoxy hybrid resins as a function of resin composition and fiber surface treatment. *J Mater Sci* 2005;40(21):5609-5618.
- [22] Szabo JS, Karger-Kocsis J, Gryshchuk O, Czigany T. Effect of fibre surface treatment on the mechanical response of ceramic fibre mat-reinforced interpenetrating vinylester/epoxy resins. *Compos Sci Technol* 2004;64(10):1717-17234.
- [23] Meszaros L, Turcsan T. Development and mechanical properties of carbon fibre reinforced EP/VE hybrid composite systems. *Period Polytech Mech* 2014;58(2):127-133.
- [24] Jang J, Lee C. Performance improvement of GF/CF functionally gradient hybrid composite. *Polym Testing* 1998;17(6):383-394.
- [25] Jarukumjorn K, Suppakarn N. Effect of glass fiber hybridization on properties of sisal fiber–polypropylene composites. *Compos Part B-Eng* 2009;40(7):623-627.

- [26] Wisnom MR, Czél G, Swolfs Y, Jalalvand M, Gorbatiikh L, Verrpoest I. Hybrid effects in thin ply carbon/glass unidirectional laminates: Accurate experimental determination and prediction. *Compos Part A-Appl S* 2016;88:131-139.
- [27] Summerscales J, Short D. Carbon fibre and glass fibre hybrid reinforced plastics. *Composites* 1987;9(3):157-166.
- [28] Pitkethly MJ, Bader MG. Failure modes of hybrid composites consisting of carbon fibre bundles dispersed in a glass fibre epoxy resin matrix. *J Phys D Appl Phys.* 1987;20(3):315-355.
- [29] Dong C, Sudarisman, Davies IJ. Flexural properties of E glass and TR50S carbon fiber reinforced epoxy hybrid composites. *J Mater Eng Perform* 2013;22(1):41-49.
- [30] Molnar K, Kostakova E, Meszaros L. The effect of needleless electrospun nanofibrous interleaves on mechanical properties of carbon fabrics/epoxy laminates. *Express Polym Lett* 2014;8(1):62-72.
- [31] Sarasini F, Tirillo J, Valente M, Valente T, Cioffi S, Iannace S, Sorrentino L. Effect of basalt fiber hybridization on the impact behavior under low impact velocity of glass/basalt woven fabric/epoxy comp. *Compos Part A-Appl S* 2013;47(1):109-123.
- [32] Dong C, Davies IJ. Flexural and tensile moduli of unidir. hybrid epoxy composites reinforced by S-2 glass and T700S carbon fibres. *Mater Design* 2014;54:893-899.
- [33] Yu H, Longana LM, Jalalvand M, Wisnom RM, Potter KD. Pseudo-ductility in intermingled carbon/glass hybrid composites glass hybrid composites. *Compos Part A-Appl S* 2015;73(1):35-44.
- [34] Sims DF, Wilson HE. Distribution of shearing stresses in a composite beam under transverse loading. *Composites* 1987;9(3):185-191.
- [35] Gryshchuk O., Karger-Kocsis J. Influence of the type of epoxy hardener on the structure and properties of interpenetrated vinyl ester/epoxy resins. *J Polym Sci A1* 2004;42(21):5471-5481.
- [36] Lee SM. Mode II Interlaminar crack growth process in polymer matrix composites. *J Reinf Plast Comp* 1999;18(13):1254-1266.

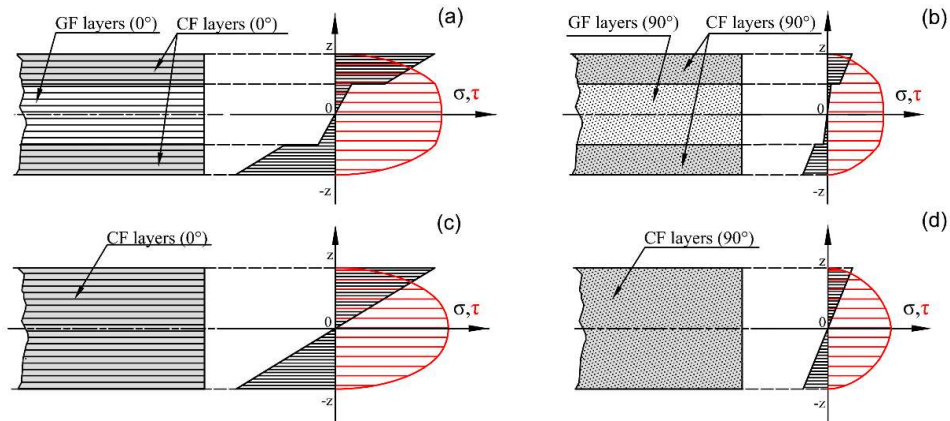


Figure 1 Theoretical flexural stress distribution of 0° (a, b) and 90° (c, d) oriented CF and CF/GF reinforcement, (compression/tensile moduli presumed equal), based on [34]

Designation	Mixing method	Resin ingredients [wt%]			Fibre content [V%]	Layers CF/GF/CF
		EP	UP	VE		
EP/CF	neat resin (-)	100	0	0	45.6 ± 1.6	3/0/3
UP/CF		0	100	0	45.4 ± 1.7	
VE/CF		0	0	100	46.7 ± 1.5	
EP/UP/A/CF	simultaneous (A)	50	50	0	46.9 ± 1.8	
EP/VE/A/CF		50	0	50	45.8 ± 2.1	
EP/UP/B/CF	sequential (B)	50	50	0	46.4 ± 1.1	
EP/VE/B/CF		50	0	50	45.9 ± 0.9	
EP/CF/GF	neat resin (-)	100	0	0	39.4 ± 2.2	2/2/2
UP/CF/GF		0	100	0	39.1 ± 2.4	
VE/CF/GF		0	0	100	40.1 ± 1.8	
EP/UP/A/GF/CF	simultaneous (A)	50	50	0	39.6 ± 1.9	
EP/VE/A/GF/CF		50	0	50	39.1 ± 1.5	
EP/UP/B/GF/CF	sequential (B)	50	50	0	40.7 ± 0.9	
EP/VE/B/GF/CF		50	0	50	40.3 ± 0.8	

Table 1 Nomination and parameters of investigated materials

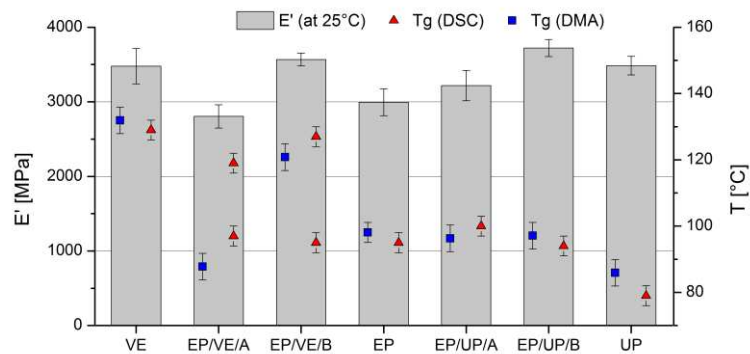


Figure 2 Storage modulus (E') at 25°C and T_g values of the investigated neat and hybrid resins

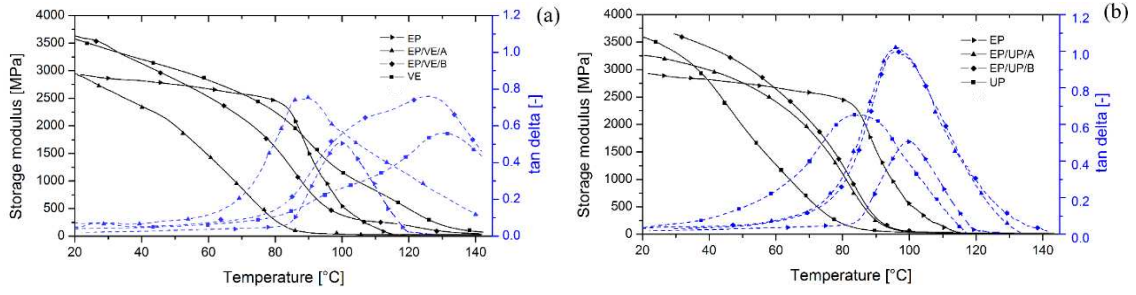


Figure 3 DMA curves of the investigated EP/VE (a) and EP/UP (b) systems

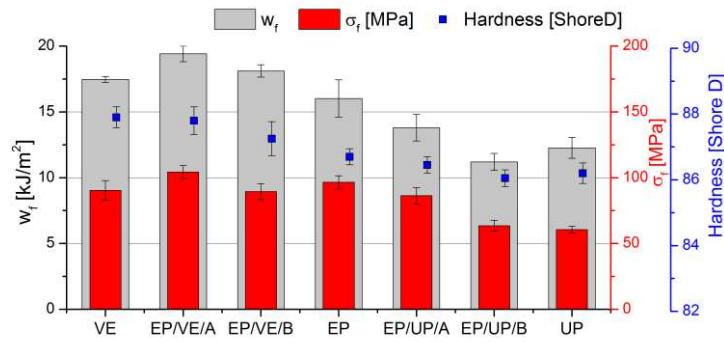


Figure 4 w_f , σ_f and surface hardness of the investigated neat and hybrid resins

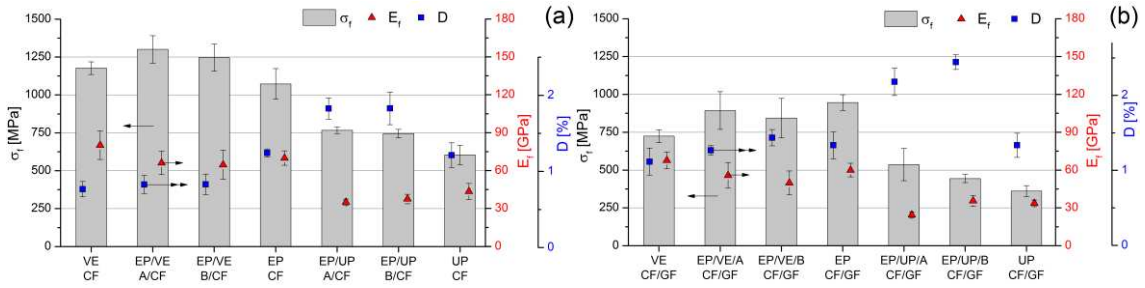


Figure 5 σ_f , E_f and D of 0° loaded CF (a) and CF/GF (b) reinforced composites

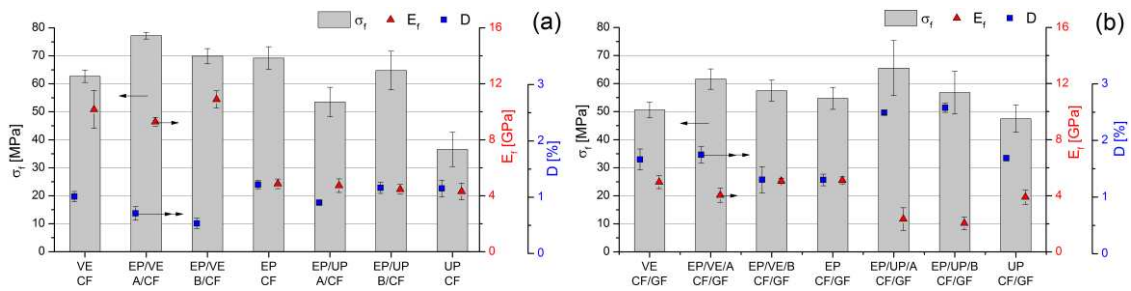


Figure 6 σ_f , E_f and D of 90° loaded CF (a) and CF/GF (b) reinforced composites

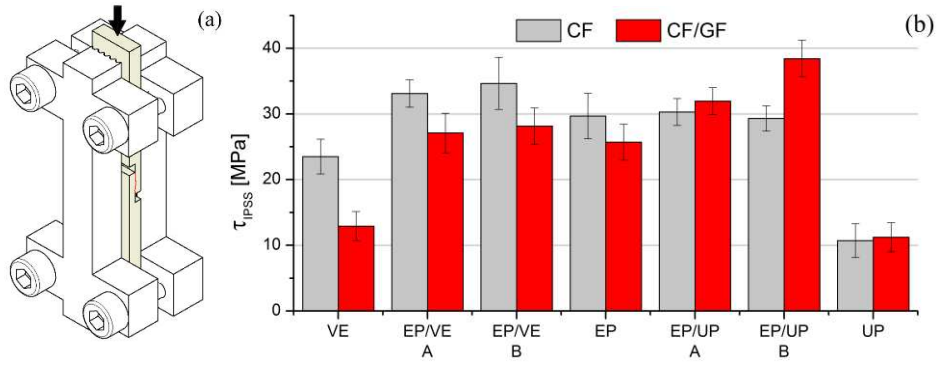


Figure 7 IPSS adjustment (a) and the IPSS results of the investigated materials (b)

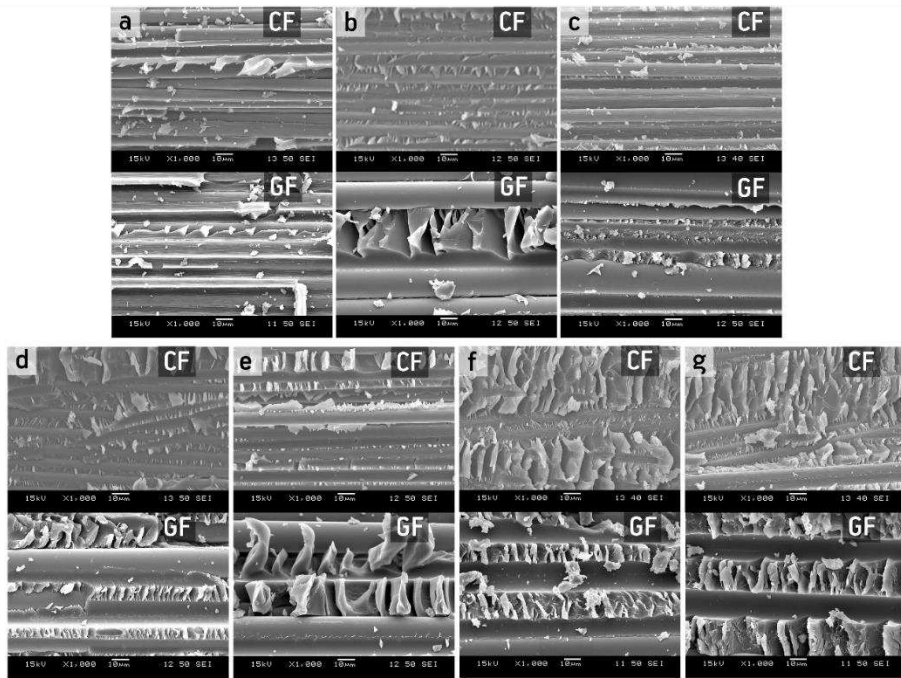


Figure 8 SEM fractographs of ILSS specimens, VE (a), EP (b), UP (c), EP/VE/A (d), EP/VE/B (e), EP/UP/A (f), and EP/UP/B (g), CF (top) and CF/GF (bottom)

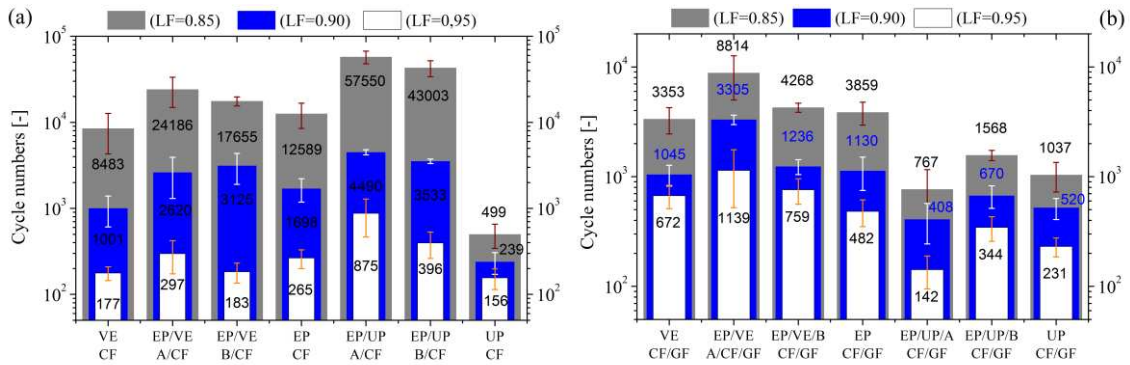


Figure 9 Flexural fatigue results of CF (a) and CF/GF (b) reinforced composites