

## IMPROVING THE COMPATIBILITY OF MAN-MADE FIBRE REINFORCED COMPOSITES

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Composites are made of two or more different materials which constitute the modernest family of construction materials for technical applications. Fibre reinforced composites are unique materials and are heterogeneous in composition. High strength/weight ratio is characteristic for them which is advantageous in many points of view. E.g. cost for moving them is much more lower than for conventional materials, they are advantageous environmentally either, do not need high maintenance costs and allow high creativity in shapes and functions.

For properties of fibre reinforced composites interaction between the fibres and the matrix is especially important beside the mechanical properties of the building parts. As their chemical compositions significantly differ from each other the proper adhesion could be achieved by application of compatibility improving so called compatibilizing additive which is able to connect either to the fibres or the matrix due to its chemical composition.

Such compatibilizing additives were produced, which are able to solve or at least reduce the incompatibility problem in carbon fibre reinforced thermoplastic and glass fibre reinforced thermoset composite systems.

**Keywords:** reinforced composites, carbon fibre, glass fibre, thermoplast, thermoset

### Introduction

A lot of new construction materials, characteristically combined materials or composites have appeared in car industry and other areas. In case of these materials one of the properties is advantage but another one is disadvantage in the point of view of application. In homogenous metals improving the strength involves high weight increase which may considerably increase investment and operational costs. Composites especially polymer composites may mean the solution for that problem according to the extent of progress. That could be traced back to the availability of polymers in great volumes at low prices and to the excellent properties (good resistance against corrosion, advantageous strength/weight and stiffness/weight ratios...) of composites made of them. So they are getting to substitute conventional construction materials (e.g. steel, aluminium) in many fields due to their high strength, stiffness and low weight.

Improving the properties of composites can be obtained by combination of two or more continuous phases. In fibre reinforced composites the phases strengthen each others effect due to the interaction between the fibres and the matrix compensating the worse properties of the clean components. The compatibility of the matrix and the reinforcing material

plays an important role during processing. Reducing the incompatibility problems compatibilizing additives are used that can help to considerably enhance the fibre-matrix interaction both in chemical and in physical ways. In literature mainly such publications are to be found that discuss the reducing of the incompatibility of the thermoplastic fibre reinforced polymers [1-6] and only a few are about the fibre-matrix interaction in fibre reinforced thermoset composites [7-8] because such problems come up much more rarely in the latter systems.

In quite lots of cases when reinforcement and thermoplastics are used together the properties of composites became worse without coupling agent that is presumed to be the cause of the incompatibility of the constitutive. In fibre reinforced thermoplastics maleic-anhydride-grafted-polyolefins (MA-g-POs), with molecular weights similar to the base plastics, are generally applied. The presence of plasticizing components retained in the MA-g-PO additives after grafting process is the main problem so the compatibilisation can be improved but plasticizing effects also occur besides.

In case of reinforced thermoset composites different silane type agents, titanates and zirconates are generally used [9] as coupling agent or fibre surface modifying agent. Those additives can connect the matrix to the fibres with hydrogen or even covalent bonds [10], so they have great effects on improving the adhesion between the components. Organosilanes are the most

widely used coupling agents for improvement of the interfacial adhesion in glass reinforced materials. According to literature their effectiveness depends on among others the nature and pre-treatment of the substrate, the type of silane used, the thickness of the silane layer and the process by which it is applied [10-11].

In our experimental work incompatibility problems of carbon and glass fibre reinforced polymer composites have been investigated. Thermoplastic and thermoset polymers have either been applied as matrices and as compatibilizing additive such experimental surface modifier additives (polyalkenyl-poly-maleic-anhydride-ester, polyalkenyl-poly-maleic-anhydride-amide and polyalkenyl-poly-maleic-anhydride-ester-amide) have been used that were produced according to our prior experiments and researches.

### Materials and processing

For carbon fibre reinforced thermoplastic composites commercially available polyethylene (Finathen 6006 PE) and PANEX®35 type carbon fibres ( $\sigma_t = 3800$  MPa;  $\epsilon_t = 242$  GPa;  $\rho = 1,81$  g/cm<sup>3</sup>;  $\text{Ø}d = 7,1$   $\mu\text{m}$ ) supplied by Zoltek Plc. were used. Geogrids applied in dam strengthening were produced at Rex International Ltd.

For glass fibre reinforced thermoset composites E-type chopped glass fibre mat with 450 g/m<sup>2</sup> specific density (supplied by former VETROTEX, now Owens Corning) and polyester (AROPOL M105 TB, (Ashland Inc., USA)) were applied. Sample sheets were made from the chopped glass fibre mats and polyester at Balatonplast Ltd. by hand lay-up laminating technique.

Before application, the reinforcing fibres and chopped glass fibre mats were impregnated with the solution of the experimental compatibilizing additives produced at University of Pannonia, Institute of Chemical and Process Engineering, Department of Hydrocarbon and Coal Processing. For carbon fibre treating polyalkenyl-poly-maleic-anhydride-ester-amide (AMAEA) type compatibilizer, for chopped glass fibre mats polyalkenyl-poly-maleic-anhydride-ester (AMAE), polyalkenyl-poly-maleic-anhydride-amide (AMAA) and polyalkenyl-poly-maleic-anhydride-ester-amide (AMAEA) agents were used.

### Experimental results

#### *Carbon fibre reinforced polyethylene composites*

Resistance against tensile stresses and relaxation tests of specimens cut out from the geogrid were determined with an INSTRON 3345 universal tensile testing machine. In case of carbon fibre reinforced polyethylene grid three characteristic directions were defined: process direction, perpendicular to process direction and diagonal direction (Fig. 1). It is important because the grid is exposed to stresses in different directions during its application.

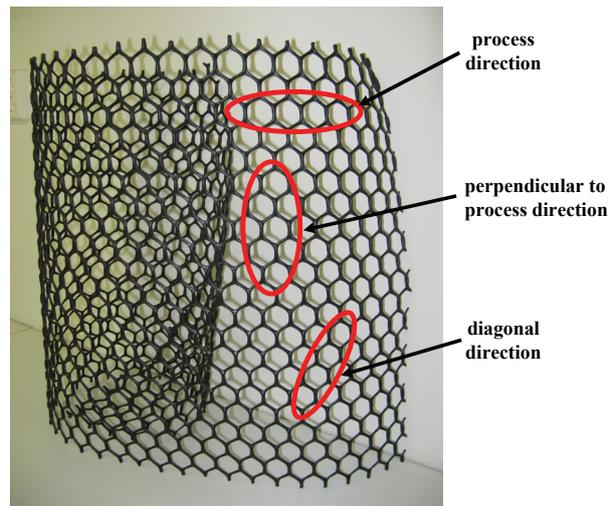


Figure 1: Testing directions of geogrid

Tested geogrid samples contained experimental polyalkenyl-poly-maleic-anhydride-ester-amide treated carbon fibres in 0%, 1%, 2% and 5% concentrations. In case of long carbon fibre reinforced thermoplastic composites fibres could not be introduced into the polymer matrix without additive treating neither by injection moulding nor by extrusion. Therefore, the properties of geogrids containing additive treated carbon fibres were compared to the properties of commercially available product containing no carbon fibres. Carbon fibres could be easily introduced into the polymer by extrusion when the fibres were treated with our compatibilizing agent and the fibres respectively remained in long fibre form ( $l = 3-4$ mm).

Tensile strength, modulus and elongation values of the geogrid in the different directions were shown in Table 1. Tensile strengths and elongations differed within the error of measurement in case of samples containing no and 1% carbon fibres in all testing directions but the differences in tensile modulus were enormous in diagonal direction. The mechanical properties of the simple tensile tests of the additive treated carbon fibres containing composites showed upward tendency compared to the unreinforced samples.

With the relaxation tests the process of shape-restitution was investigated at three different loads (100 N, 200 N and 300 N). Relaxation curves of specimens, perpendicular to process direction, at 200 N load was shown in Fig. 2. Fig. 3 showed the load values after 180 sec relaxation in case of the different loads and different directions. Relaxation of the specimens did not show significant tendencies, the results changed within the error of measurement. The load values at given time after the load passed off did not show significant differences in the various specimen directions. The decrease of load fell down from ~45% to ~30% with increasing relaxation load. Only the specimens perpendicular to process direction made from the virgin polymer and the specimens in process and perpendicular to process direction made from the 1% carbon fibre containing composites could be measured at 300N relaxation load, the others could not bear the applied relaxation stress.

Table 1: Mechanical properties of geogrid in the different specimen directions

		Tensile strength at	Maximum tensile	Tensile modulus
		max. tensile elongation	elongation	
		MPa	mm	MPa
0% carbon fibre	p.d.	23.3±1.1	8.2±0.4	15.1±1.8
	p.p.d.	35.0±0.7	13.0±0.5	45.1±0.8
	d.d.	25.0±1.4	10.5±0.5	24.8±0.5
1% carbon fibre	p.d.	24.0±1.2	8.1±0.5	15.3±1.6
	p.p.d.	35.0±0.6	12.8±0.5	43.4±0.3
	d.d.	22.7±1.1	11.2±0.6	29.4±0.4
2% carbon fibre	p.d.	30.0±0.8	8.2±0.5	16.0±0.3
	p.p.d.	34.4±0.6	14.6±0.3	34.2±1.2
	d.d.	9.5±0.9	18.0±0.5	36.0±0.4
5% carbon fibre	p.d.	31.3±0.4	8.5±0.3	15.0±0.2
	p.p.d.	25.8±0.3	14.5±0.3	54.9±1.5
	d.d.	12.8±0.7	18.3±0.2	42.8±0.3

p.d.– process direction, p.p.d.– perpendicular to process direction, d.d.– diagonal direction

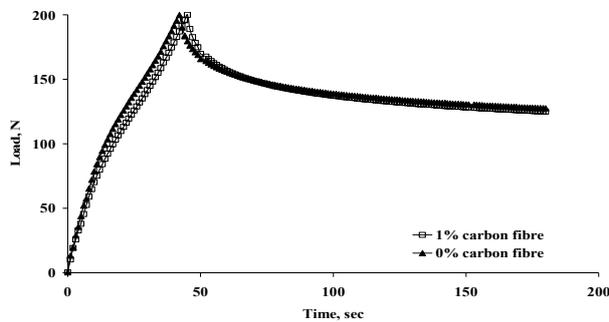


Figure 2: Relaxation curves (at 200N relaxation load, specimens perpendicular to process direction)

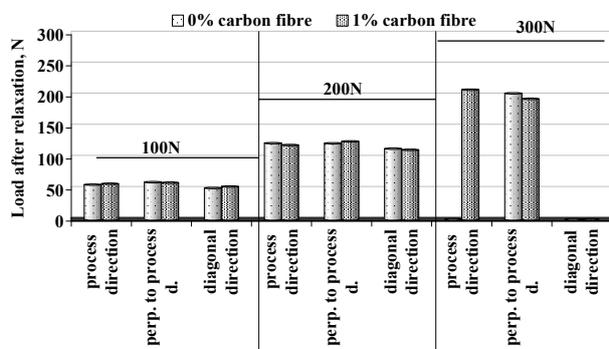


Figure 3: Results of relaxation tests

After simple tensile tests different fatigue conditions were applied and tensile properties were also determined. According to relaxation tests two different loads (100 N and 250 N) and three different numbers of cycles were used during fatigue tests then tensile properties were measured. 50, 100 and 150 numbers of cycles were applied in case of 100 N and 100 numbers of cycles at 250 N pre-load at 90 mm/min crosshead speed. Results of fatigue tests were shown in Figs 4-7.

As the Figs 4 and 5 showed significant differences were experienced in case of tensile strengths in the various specimen directions. Rising tendency could be observed comparing to the results of fatigue tensile tests, however, the specimen direction also influenced the differences between the polymer and the 1% carbon

fibre containing composite. The differences varied within the range of 0.5-29.7%. The worst results were experienced with specimens in process direction either as in case of simple tensile tests. Tensile strength of 1% carbon fibre containing composites decreased with the numbers of pre-cycles in each direction which is probably because fibre orientation can not compensate the stress after a given degree of pre-stress. Tensile strength of the virgin polymer slightly increased with numbers of cycles which was probably due to the higher elasticity of the polyethylene than of the carbon fibre reinforced composites.

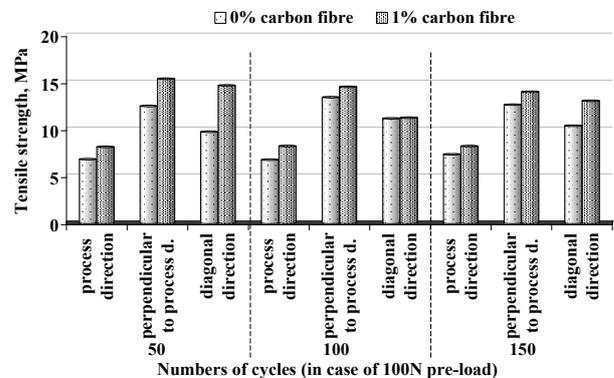


Figure 4: Results of fatigue tests in the different specimen directions

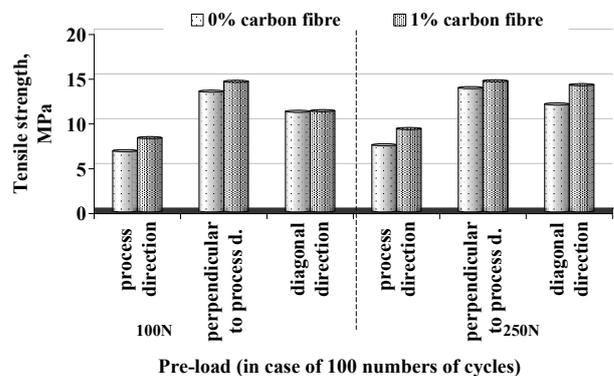


Figure 5: Results of fatigue tests in the different specimen directions

A further advantage of the carbon fibre reinforced composites was that better tensile strength could be measured with applying pre-stress compared to the results of the grid made of polyethylene where application of pre-stress decreased the tensile strengths of the specimens in each direction. That phenomenon was probably due to fibre orientation. The highest increase was observed with specimens in diagonal direction. Similar results were obtained with the other properties (tensile elongation, modulus, properties at break) in fatigue tests.

The effects of fibre content on the fatigue properties were also examined. According to *Figs 6-7* tensile strength increased when the fatigue conditions became stricter in case of higher carbon fibre content. A decrease could be observed in case of 2% carbon fibre content compared to 1% carbon fibre content which was probably due to processing failure as the specimens showed the trends described in the previous paragraphs.

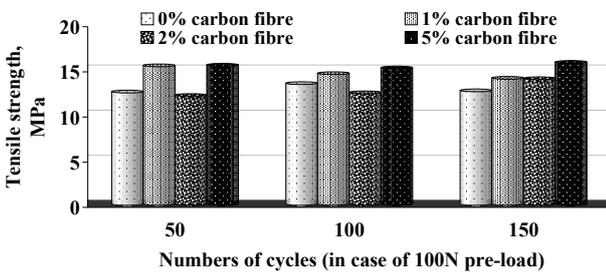


Figure 6: Results of fatigue tests in case of different carbon fibre content

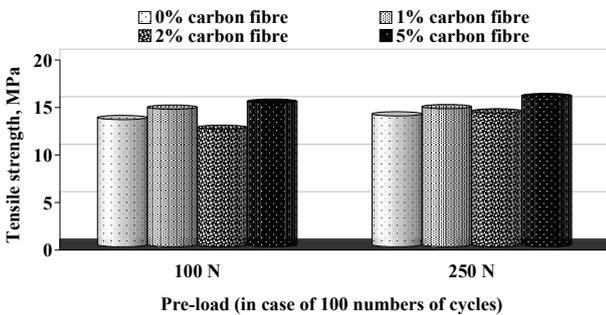


Figure 7: Results of fatigue tests in case of different carbon fibre content

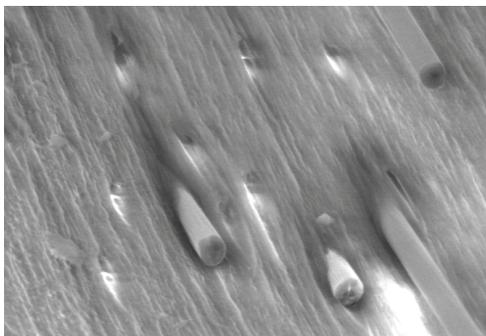


Figure 8: SEM graph of the fractured surface of the 5% carbon fibre containing composite

Fibre-matrix interaction was followed by Scanning Electron Microscopy. *Fig. 8* showed the fibre-matrix connection and represented that the fibres were just

broken at the surface and fibre-pullout was not experienced so the additive could establish good connection between the elements.

*Chopped glass fibre mat reinforced polyester composites*

Results of tensile tests were shown in *Figs 9-11* while Charpy impact properties in *Fig. 12*. Tensile properties of the samples were determined according to MSZ EN ISO 527-1-4:1999 and Charpy impact properties according to ISO 179-2:1997 standard.

As glass fibre content can considerably influence the mechanical properties glass fibre contents of the samples were determined. Measurements were carried out according to MSZ EN ISO 3451-1:1999 standard so ash contents were measured after 800 °C heating. The glass fibre contents of the samples with and without additive were 35.5±2.4%.

*Fig. 7* showed tensile strength at break. Properties at maximum tensile elongation and at break were the same because of the physical characteristics of the polyester composites. During the mechanical tests the samples showing the best properties were compared to the reference samples.

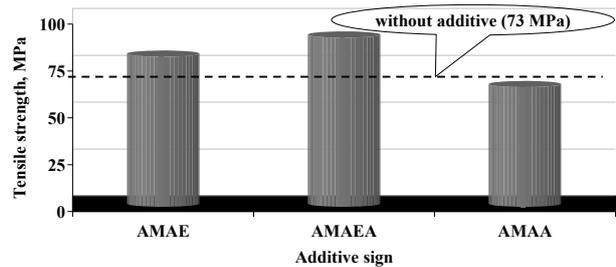


Figure 9: Changes in tensile strength

According to the results of tensile tests it could be stated that such surface modifier additive could be produced with which better mechanical properties could be realized than with untreated fibres reinforced composites. Tensile strength was 9.7% better with AMAE additive, and 23.7% better with AMAEA than the tensile strength of the untreated fibres containing composite. But with AMAA additive the tensile strength decreased with almost 13% which showed that the high nitrogen-content and the absence of ester groups influence the fibre-matrix interaction disadvantageously.

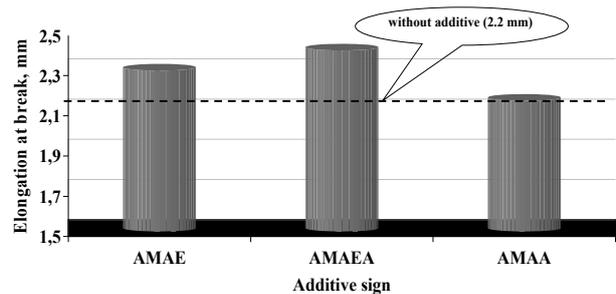


Figure 10: Changes in elongation at break

Similar results were obtained in case of elongation at break either where the positive changes were 4.5% and 9.1% but in case of AMAA agent with 2.3% lower value of elongation could be observed.

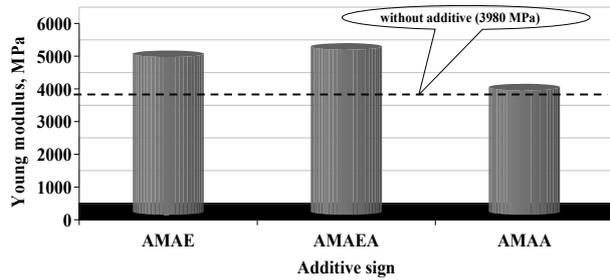


Figure 11: Changes in Young-modulus

Young-modulus increased with almost 27% applying the AMAEA additive but in case of the additive containing no ester groups 4% decrease was experienced compared to the reference sample.

Dynamic tests were carried out with a CEAST Resil Impactor machine according to the ISO 179 standard using A type cut specimens. As Fig. 12 showed in the first two cases the specific work was 16.5% and 20.6% higher than without additive. With the third additive that property decreased with 3%.

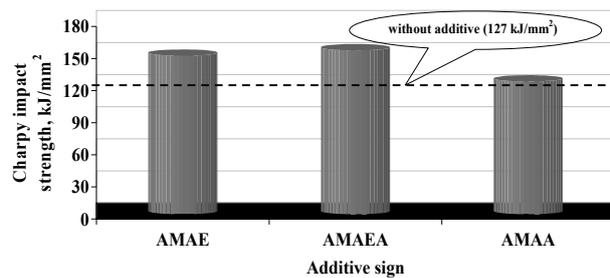


Figure 12: Changes in Charpy impact strength

The broken samples were examined because the fibre pull-out is the most visible in that case. Figs 13-15 represented the fibre-matrix interaction shown on the SEM graphs. In case of untreated fibres containing composites the matrix covered the fibres in many places (Fig. 13) but at the fractured faces the fibres separated from the matrix.



Figure 13: Fibre-matrix interaction in untreated chopped glass fibre mat reinforced polyester composites

According to the SEM graph about the samples showing best mechanical properties (Fig. 14) the compatibility of the glass fibres and matrix was improved because the fibres pulled out less from the matrix and were broken at the surface, and the surface was covered with the polymer even after break in many places.

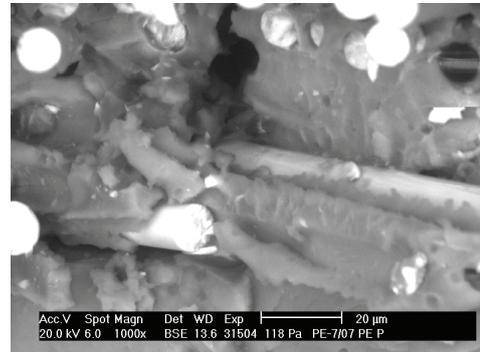


Figure 14: Fibre-matrix interaction in chopped glass fibre mat reinforced polyester composites applying AMAEA compatibilizing additive

Fig. 15 showed the fractured face of the samples showing worse mechanical properties where it can be seen that the surface of the glass fibres became smooth because they separated easily from the matrix. The glass fibre bundles functioning as reinforcing materials easily moved out from the starched resin so they could not supply their objectives.

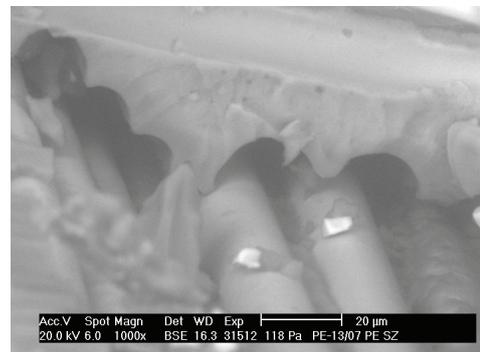


Figure 15: Fibre-matrix interaction in chopped glass fibre mat reinforced polyester composites applying AMAA compatibilizing additive

### Summary

With our compatibilizing additives the mechanical properties of carbon fibre reinforced thermoplastic and glass fibre reinforced thermoset composites could be enhanced.

Applying our experimental compatibilizing additive carbon fibre reinforced geogrid could be produced by extrusion. While the mechanical properties of the additive treated carbon fibres containing composites did not show significant difference compared to the virgin polymer in case of simple tensile tests considerable differences were experienced in case of fatigue properties.

Either with increasing pre-load or with numbers of cycles deteriorative trends could be marked in case of unreinforced geogrid samples in opposition with the carbon fibre reinforced ones where the rising tendency was probably due to the orientation of the fibres. Convenient adhesion was developed in the composites as SEM graphs proved.

According to the tensile and dynamic mechanical properties of compatibilizing additive impregnated chopped glass fibre mat reinforced laminated polyester composites such compatibilizing additive could be produced by which better mechanical properties could be achieved than the untreated glass fibre reinforced composites. Fibre- matrix adhesion was investigated by SEM in glass fibre reinforced composites either. In untreated fibres containing systems there are places where convenient adhesion was developed between the fibres and the matrix so the resin surrounded the fibres well but somewhere the components separated. The resin adhered to the fibres even after break in case of effective additive as represented on the SEM graphs.

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