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Final Report

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Mechanical behavior of nanoparticle containing hybridcomposites in case of cyclic load

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1. Introduction

Performance improvement is one of the most important criteria when a novel polymer composite is developed for engineering applications. To extend mechanical performance of materials composite industry uses several types of reinforcing materials. The popularity of glass fibers is unbroken, but nowadays carbon fibres and basalt fibres are gathering ground. Although traditional, two-phase composites are still being developed, more and more researchers think that using an additional third phase might be an effective way to increase the mechanical performance of a composite or endow it with functional properties. This third phase can be nano-sized materials that have good complementary effect on the properties of the composites. These three phase composites are usually called hybridcomposites. It is also important for a new engineering material that it has to be easily insertable into the manufacturing processes. As mass production technologies are preferred in the industry thermoplastic matrix was chosen. Before the final decision according to the matrix type there were some experiments in case of thermoset matrices [1][2][3][4][5][6]. Based on the results the size-effect (macro-nano scale) of the materials was better understood.

In the last decade the appearance of graphene presented challenges for researchers in the field of composites, too. Beside the unique electrical and thermal properties, graphene has the greatest tensile strength and modulus among the known materials and it has extremely high aspect ratio.

Based on the literature review graphene (GnP) was chosen as nano-sized reinforcing material to make nano-, and hybrid composites. For micro-sized reinforcement basalt fibers (BF) and was chosen and polyamide 6 (PA 6) as matrix material since it is a widely applied engineering plastic in the field of thermoplastic composites. There were also produced carbon nanotube and montmorillonite containing composites, and carbon fiber was also applied as micro-size reinforcement [7][8][9][10]. Even if the results of their investigations showed new scientific result it also turned out that the graphene containing basalt fiber reinforced hybrids has greater potential therefore this composites were deeply investigated [11][12][13]. It should be mentioned, that at the materials selection their fatigue properties were also taken into consideration (the hydraulic wedge grips were financed by the project).

Polymer composites in automotive industry usually suffer cyclic loads, that is why it is important to investigate new types of composite cyclic properties. The positive effects of conventional fiber reinforcement on static and dynamic properties of polymers are well known and deeply examined. In case of hybridcomposites the researchers dealt mainly with the static-mechanical behaviour till now, but the response on cyclic load is less investigated, however the mechanical load is usually not static. Even if the load is static or dynamic the response of the material originates in its structure *ergo* there has to be connection between them.

For the qualification of the mechanical behaviour of the produced materials conventional quasi-static methods, and fatigue test were applied. There were carried out also quasi-static cyclic mechanical tests, that could help to reveal the deformation components of the material. These components originates in the structure of the materials, therefore can help to reveal the structure-mechanical behaviour relationships.

Beside these mechanical investigations morphological ones were also carried out as the presence of nanoparticles and microfibers could have different effects on it.

2. Materials and methods

Materials

Schulamid 6 MV 13 type polyamide 6 (PA 6) from A. Schulman GmbH (Germany) was used as matrix material. BCS KV12 type basalt fiber (BF) from Kamenny Vek Ltd. (Russia), and Panex 35 Type 95 carbon fiber (CF) from Zoltek Zrt. (Hungary) were applied as reinforcement. Graphene xGnP® graphene nanoplatelets - Grade H (GnP) supplied by XG Sciences, Inc. (USA) were used as nano-sized reinforcement.

Sample preparation

A Labtech Scientific type twin screw extruder (L/D=44; D=26 mm) was used for continuous melt mixing. The screw speed was 25 1/min and the extrusion temperature was 250°C. Dried PA 6 granulates (80°C; 4 hours) were mechanically mixed with the reinforcing materials, then extruded and granulated (particle size: 4.5 mm). Dumbbell type specimens (4x10 mm cross section) were injection molded (injection molding temperature was 275°C, mold temperature was 80°C, and maximal pressure was 800 bar) on an Arburg Allrounder Advance 370S 700-290 injection molding machine. For the composite preparation 0.25; 0.50; 0.75 and 1.00 wt% graphene was used.

Characterization methods

Before the mechanical tests, the specimens were conditioned at 50% relative humidity and 25°C for a month. Tensile tests were performed on a Zwick Z020 universal testing machine according to EN ISO 527.

Before the fatigue tests high speed tensile tests (crosshead speed: 200 mm/min) were performed to determine the load levels.

Fatigue tests were carried out on an Instron 8872 hydraulic tensile testing machine equipped with Instron 2742-301 type hydraulic grips. The load-controlled fatigue tests were performed under tension-tension load with sinusoidal waveform. The excitation frequency was 2 Hz and the load factor was R=0.1 (R=maximum stress/minimum stress) (Fig.1.). The temperature of the specimen surface was measured with a FLIR A325sc infrared camera. During the tests, the area of the whole surface was inspected and the highest temperature was registered.

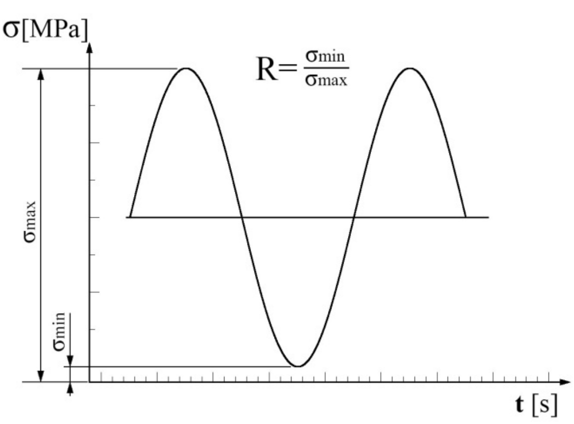


Fig. 1. Tension-tension fatigue test load as a function of time

The fracture surfaces of the broken tensile and fatigue tested specimens were investigated with a Jeol 6380 LA type scanning electron microscope (SEM) after sputtering them with a thin gold layer.

When a polymer is mechanically loaded fundamentally three different types of deformation awakes: instantaneous elastic (energy-elastic), time-dependent viscoelastic (entropy-elastic) and time-dependent viscous (relaxation) deformation. The first two components together are elastic deformations. The composites can be used as structural material until these elastic deformations are overwhelmingly dominant compared to the viscous one. The characterization of the deformation components is quite difficult as they depend on several parameters like the applied load or the loading time. Therefore the researchers introduced the rate of the elastic recovery. This can be calculated from a cyclic measurement where the tensile load is increased by the cycles but between each cycle a certain time is applied for the recovery of the time-dependent viscoelastic deformation. The elastic recovery can be calculated by the ratio of the elastic deformation and the total deformation. As it is shown in Fig. 2. the plastic deformation is a cumulative parameter since in this case the reference point is always the zero-point independently from the value where the current cycle begins. The end of the elastic region can be indicated by a significant change in this parameter during the cyclic test. Another possibility is to give the designers a maximum viscous deformation as a set-point for sizing.

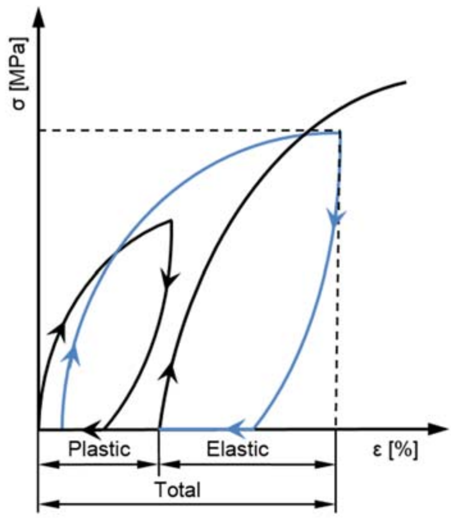


Fig. 2. Strain-stress curves for cyclic loading, at increasing load levels (the blue colored curve signs a complete cycle)

The cyclic tensile tests were performed also on Zwick Z020 universal testing machine machine. The relaxation time was set to be 30 s and the load was increased by 100 N in each cycle. The machine was used in force-controlled mode, the up and the down load speed was set to 100 N/s. Because of the adjustment of the machine, close to the actual target force within a cycle an approaching procedure begins of which original purpose is to avoid the overshot of the force. This means that in case of thermoplastic polymers at relative high loads the role of the viscous deformation becomes more observable. From a tensile tester point of view it means that it takes more time to achieve the target force. Based on these considerations the measuring procedure was set to end when at least 1 % additional elongation was detected close to the maximum force, and the force still could not achieve the maximum value. The latter phenomenon meant that the creeping behaviour began to be dominant, that is far away from the elastic deformations.

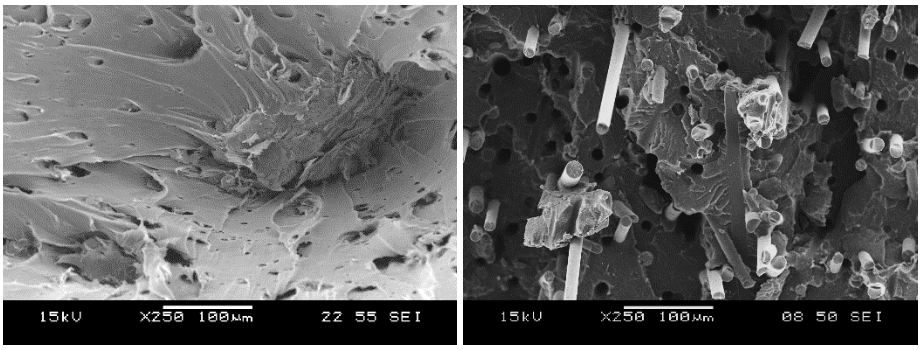
3. Results and discussion

The tensile strengths, tensile moduli and elongation at break values are tabulated in Table 1. The addition of graphene induced some enhancement in the tensile moduli but the effect was less dominant for higher filling rates. The elongation at break decreased when graphene was incorporated. At 0.25 GnP content the decrease was less compared to the other nanocomposites. The presence of basalt fiber significantly increased the tensile strengths and modulus values compared to the neat matrix and the nanocomposites and decreased the elongation at break. In case of hybrid composites, there was no significant change in strength compared to the basalt fiber reinforced one, but graphene notably enhanced Young's modulus, and that refers to better nanoparticle dispersion.

Materials	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]
PA 6	56.9 ± 0.7	2054 ± 17	53.5 ± 14.1
PA 6 / 0.25 GnP	59.9 ± 0.7	2244 ± 37	18.5 ± 3.1
PA 6 / 0.50 GnP	57.5 ± 0.9	2259 ± 30	10.9 ± 2.5
PA 6 / 0.75 GnP	56.0 ± 0.9	2220 ± 28	9.9 ± 2.0
PA 6 / 1.00 GnP	53.0 ± 0.1	2123 ± 28	11.0 ± 3.4
PA 6 / 30 BF	99.0 ± 0.3	4419 ± 154	5.1 ± 0.1
PA 6 / 30 BF / 0.25 GnP	101.6 ± 0.9	4917 ± 24	4.8 ± 0.2
PA 6 / 30 BF / 0.5 GnP	99.9 ± 0.2	4902 ± 124	4.7 ± 0.2
PA 6 / 30 BF / 0.75 GnP	95.8 ± 0.7	4872 ± 108	4.5 ± 0.2
PA 6 / 30 BF / 1.00 GnP	94.1 ± 0.6	4858 ± 82	4.4 ± 0.1

Table 1. Tensile properties of graphene containing PA 6 nanocomposites

In order to examine if nanoparticle dispersion was successful, scanning electron microscope images were prepared from the fracture surfaces. Large aggregates could be found on the surface of nanocomposites (Fig 3. a.).



a) b)

Fig. 3. Fracture surfaces of tensile tested composites:
a) PA6 / 0.25 GnP; b) PA 6 / 30 BF / 0.25 GnP

In case of hybrid composites such large aggregates could not be found. As it was expected, the presence of micro-fibers helped to break up the large nanoparticle aggregates, and this way better dispersion could be achieved (Fig 3. b).

For nanocomposites the cycle number connected to failure significantly decreased as nanoparticle content increased (Table. 2.). This effect can be explained by the imperfect nanoparticle dispersion that is also revealed by the tensile investigations (Table 1.)

Load [%]	PA 6	PA 6 / 0.25 GnP	PA 6 / 0.50 GnP	PA 6 / 0.75 GnP	PA 6 / 1.00 GnP
	cycles [-]	cycles [-]	cycles [-]	cycles [-]	cycles [-]
90	105 ± 13	102 ± 7	74 ± 10	55 ± 27	60 ± 7
80	232 ± 5	227 ± 24	167 ± 7	143 ± 3	139 ± 3
75	426 ±62	414 ± 14	344 ± 17	256 ± 11	279 ± 24
Load [%]	PA 6 / 30 BF	PA 6 / 30 BF / 0.25 GnP	PA 6 / 30 BF / 0.50 GnP	PA 6 / 30BF / 0.75 GnP	PA 6 / 30BF / 1.00 GnP
	cycles [-]	cycles [-]	cycles [-]	cycles [-]	cycles [-]
90	18 ± 1	24 ± 1	18 ± 2	19 ± 2	16 ± 1
80	55 ± 4	75 ± 5	60 ± 3	61 ± 14	49 ± 3
70	175 ± 19	218 ± 7	187 ±4	151 ± 19	147 ± 12

Table 2. Composites and hybrid composites fatigue life (number of cycles survived until failure)

At low graphene contents the hybrid composites showed better fatigue properties compared to the reference basalt fiber monocomposite beside relatively low standard deviations. At 0.25 wt% graphene content 30% increment was experienced in the cycles to failure values at every load level (Table 2.). Over 0.50 wt% graphene content this positive effect was not found any more.

The analysis of the awaked elongations during the fatigue test could imply important information about the structural behavior of the materials. The elongation of specimens during fatigue tests was smaller at low graphene contents compared to the values measured in case of neat polyamide 6 (Fig. 4. a). The effect was more outstanding for the nanocomposite with 0.25 wt% GnP content, where the measured values were only fractions of the elongation of the reference material. This means that cyclic creep decreased, a very important feature from an engineering design point of view.

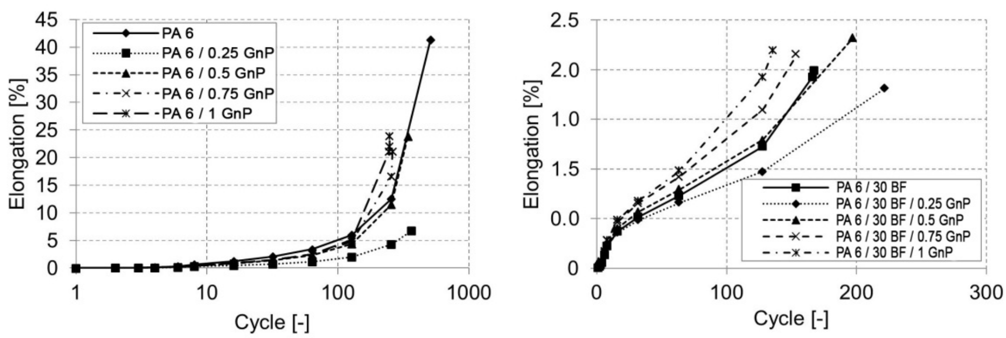
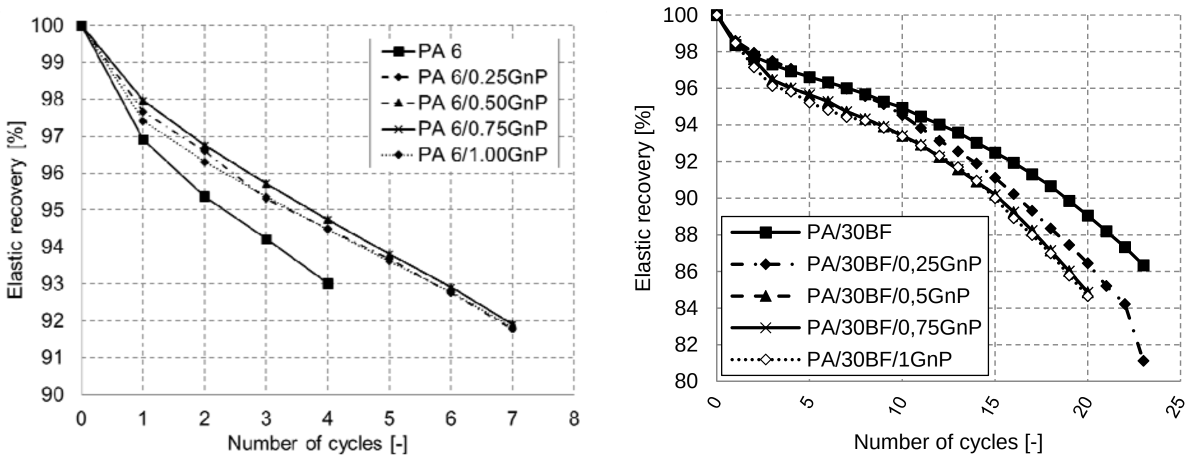


Fig. 4. Elongation as a function of cycle numbers in case of fatigue tests:
a) PA6 / GnP nanocomposites; b) PA 6 / 30 BF / GnP hybridcomposites

At hybridcomposites at 0.25 wt% graphene content, remarkable decrement in the cyclic creep values was revealed (Fig. 4. b).

It can be concluded that the presence of the graphene has dual effect. One is that at low deformations it could really change the properties of the materials (modulus increment, decreased elongation during fatigue test). But When the dispersion is not good enough than the aggregates acts as fault location therefore the initialization of the cracks is more easy that leads to early fracture (lower strength or fatigue life).

This difference has to reflect in the elastic recovery values (Fig. 5). For the nanocomposites it can be concluded that while at the quasi-static measurements the particle content affected the mechanical properties, there were not remarkable differences in case of the cyclic results. It can be explained by that for this cyclic measurements the loads were on a lower level, therefore the presence of the aggregated nanoparticles had less negative influence. This also correlates with the tensile moduli results, where moderate increments were observed compared to the matrix, but there were not significant differences as a function of nanoparticle content (Fig. 5. a).



a) b)

Fig. 5. The elastic recovery as a function of cycle numbers:
a) PA6 / GnP nanocomposites; b) PA 6 / 30 BF / GnP hybridcomposites

In case of the hybridcomposites the effect of the basalt fiber was dominant (Fig 5. b). The presence of the graphene decreased the elastic recovery. Instead of this fact there was a notable increment in the fatigue life. The solution is in the crack propagation: the well dispersed nanoparticles could hamper the crack propagation in the material that resulted in enhanced fatigue life.

To shed light on the structural causes of the enhanced fatigue life, the fracture surfaces were investigated by SEM. The evolved surfaces of hybrid composites were similar to that of basalt fiber reinforced composites as in case of all composite types the fracture surfaces can be divided into a micro ductile and a micro brittle part. Fig. 6. shows these two parts in case of PA6 / 30BF and hybridcomposite with 0.25 wt% GnP content. The failure process was the following. Firstly, the cracks appear at the end of fibers because they are stress concentration points, then the crack grows along fibers, and finally these areas of failure connect to each other and create voids. This tough breakage is dominant until a critical size is reached, when the test ends with a sudden and catastrophic rigid breakage. The presence of graphene did not change the failure process itself but it slowed down crack propagation.

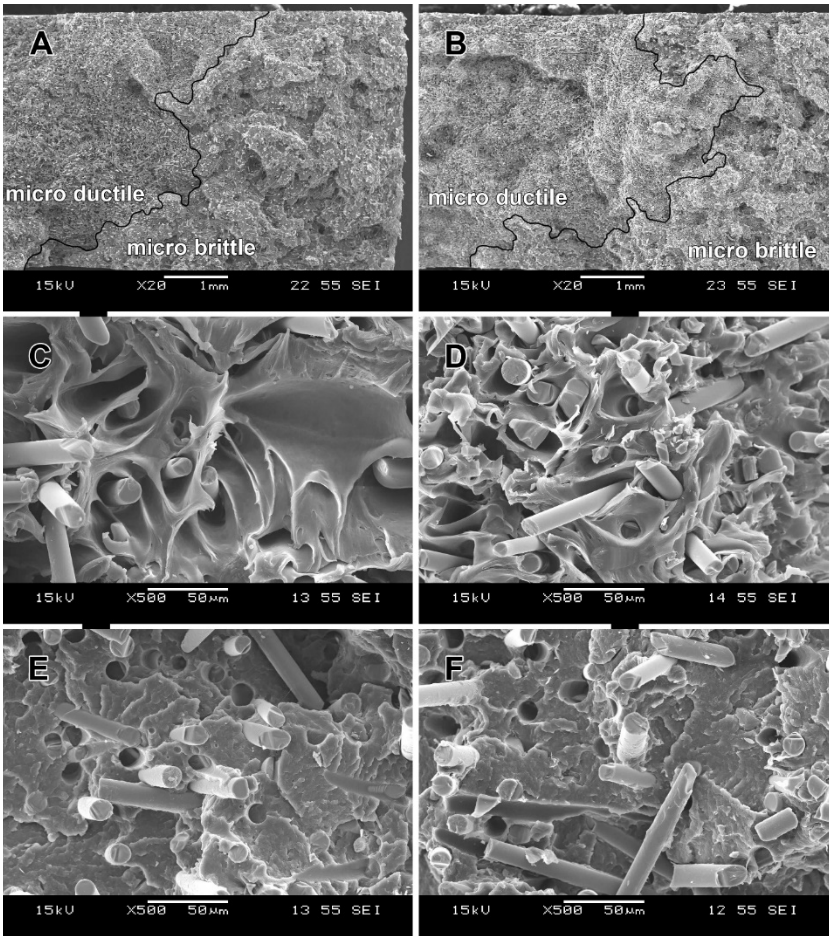


Fig. 6. Typical fracture surface of the PA6 / 30 BF composite (A, C, E) and hybrid composite with 0.25 wt% GnP content (B, D, F).

4. Conclusions

In the first part of the project the most proper material combination for the detailed investigations were chosen based on their performance (including their fatigue life). Based on these experiments numerous publications are published. For the detailed experiments PA 6 was chosen as matrix material, graphene nanoparticle as nano-sized and basalt fiber as micro-sized reinforcement. The tensile test results showed that the presence of graphene did not change the mechanical properties of composites significantly; however, in case of hybrid composites with low graphene contents some increment in the Young's modulus was exhibited. During low-cycle fatigue tests of nanocomposites with graphene content significant decrements in the fatigue life were observed. This can be explained by the high number of graphene aggregates that are observed in the SEM pictures of the cut surfaces of the specimens. In spite of the improper dispersion in nanocomposites with 0.25 wt% GnP content, the cyclic creep decreased significantly compared to the value of neat PA 6. A similar favorable effect was revealed in case of hybrid composites with 0.25 wt% GnP content, but in this case a remarkable increment in fatigue life was also exhibited at all applied load levels compared to the basalt fiber monocomposite.

5. Publications

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